



**Sonoma Technology Inc.**

SOUTHERN CALIFORNIA AIR QUALITY STUDY (SCAQs)  
PROGRAM PLAN

June 1987

STI Ref. 96030-708R  
Agreement No. A5-157-32

Prepared for:

California Air Resources Board (ARB)  
P.O. Box 2815  
Sacramento, CA 95812

3402 Mendocino Avenue, Santa Rosa, California 95401  
707/527-9372



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Prepared by Sonoma Technology Inc. (STI) and  
Desert Research Institute (DRI) with extensive input  
from the California Air Resources Board (ARB) and other  
sponsors, participants, and members of the technical  
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## ABSTRACT

This program plan outlines the measurement and management approach and reviews the technical background for the Southern California Air Quality Study (SCAQS). SCAQS is a multi-year, integrated, cooperative study which is funded by many different government agencies, industry groups, and individual corporate sponsors. This plan has been prepared with the input of the sponsors, participants, and potential users of the study data and represents a composite of their ideas.

The overall goal of SCAQS is to develop a comprehensive and properly archived air quality and meteorological data base for the South Coast Air Basin that can be used to test, evaluate, and improve elements of air quality simulation models for oxidants, PM-10, fine particles, toxic air contaminants, and acidic species. In addition, SCAQS will provide a data base which can be used to address specific technical questions regarding the emission, transport, transformation, and deposition of pollutants.

The study is planned to take place in 1987 during six weeks in early summer and four weeks in late fall. Extensive routine measurements and special studies will take place on 18 days during the study. Most of the monitoring will take place at existing air quality monitoring sites. Airborne, meteorological, and tracer measurements are planned at additional locations.

## ACKNOWLEDGEMENTS

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Without the support and financial commitments of the sponsors, this study would not be possible. These sponsors are: the Environmental Protection Agency (EPA), the South Coast Air Quality Management District (SCAQMD), the Coordinating Research Council (CRC), the Electric Power Research Institute (EPRI), the Ford Motor Company, the General Motors Research Laboratories (GMRL), the Motor Vehicle Manufacturers Association (MVMA), Southern California Edison (SCE), and the Western Oil and Gas Association (WOGA).

Many sponsors, participants, and potential users of the program data have contributed their ideas and their time for review and comment during the planning process. The list of such people is too long to include here, but many of them are listed in Appendix A. We gratefully acknowledge their contributions and recognize that the planning effort would have been impossible without their cooperation and efforts.

Several parts of the plan were prepared by other members of the STI or DRI staff and by STI consultants. The staff members and consultants who prepared parts of the plan are: Dr. L. W. Richards, STI; Dr. S. V. Hering, STI; Mr. D. E. Lehrman, STI; Dr. J. C. Chow, DRI; Dr. G. R. Cass, Caltech; and Dr. T. B. Smith.

In addition, members of the Technical Advisory Group for the project contributed ideas to the plan as well as provided continuing review of the planning effort. The members of the technical advisory group were: Dr. R. Atkinson, Dr. G. R. Cass, Dr. S. K. Friedlander, Dr. D. Grosjean, Dr. G. M. Hidy, Dr. W. B. Johnson, Dr. P. H. McMurry, and Dr. T. B. Smith.

Finally, we very much appreciate the exhaustive efforts of M. Howard, S. Duckhorn and S. Hynek who typed the text, prepared the figures, and published the drafts and final version of this plan under tight schedules.

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## 1. INTRODUCTION

### 1.1 BACKGROUND AND ISSUES

In recent years in California, the mix and spatial distribution of pollutant emissions have changed substantially, and several new classes of pollutants have gained the public's attention. In the next few years, many difficult regulatory issues relating to these changes will confront the California Air Resources Board (ARB), the Environmental Protection Agency (EPA), and the South Coast Air Quality Management District (SCAQMD). Resolution of these issues and development of effective control strategies to ameliorate California's air quality problems will require a better understanding of the relationships among the sources, receptors, and effects of the pollutants in question. This understanding can only be developed through measurement, data analysis, and modeling in an iterative fashion. Design and evaluation of alternative control strategies must be done using models which embody our best understanding of the above relationships.

This program plan outlines the first steps in a measurement, analysis, and modeling strategy which can ultimately provide the regulatory agencies with tools necessary to make effective decisions. This study, the Southern California Air Quality Study (SCAQS), addresses the following issues: ozone ( $O_3$ ),  $NO_2$  and the roles of nitrogen oxides ( $NO_x$ ),  $PM_{10}$ , fine particles, visibility, toxic air contaminants, and atmospheric acidity. The first five issues are addressed in depth, and adequate information should result from this project for the development and testing of descriptive and prognostic models. Understanding of the latter two issues will be greatly improved by this study, but this study alone will not necessarily provide the information required to develop and test prognostic models.

Although similar problems are faced by most California air basins, the focus of this study will be the South Coast Air Basin (SOCAB) since that is where the problems are most severe. Also, the SOCAB is one of the most well documented and intensively researched airsheds in the world.

Since the scope of the study is beyond the resources of the ARB alone, and since the results of the study could affect the actions of both government and industry, SCAQS has been designed as a cooperative project. Coordinated sponsorship by both government and industry should help assure adequate funding to meet the goals of the study. In addition, development of a protocol which is satisfactory to the parties affected by the results should minimize conflict about technical issues during the regulatory process.

SCAQS is designed to meet the goals and objectives agreed upon by the ARB and other potential sponsors. This program plan is the result of an open planning process which entailed extensive consultation with the modeling and measurement communities. The resulting design is an attempt to satisfy the needs expressed by the technical community to meet the stated objectives. The scope is quite large, and there obviously will be additional changes as the study evolves. The earlier version of this document (Blumenthal et al., 1986) was used as a starting point from which the final study design has been constructed. Feedback from potential sponsoring agencies and data users regarding their relative priorities and levels of resources has been used to refine the design. Lists including most of the people and organizations who

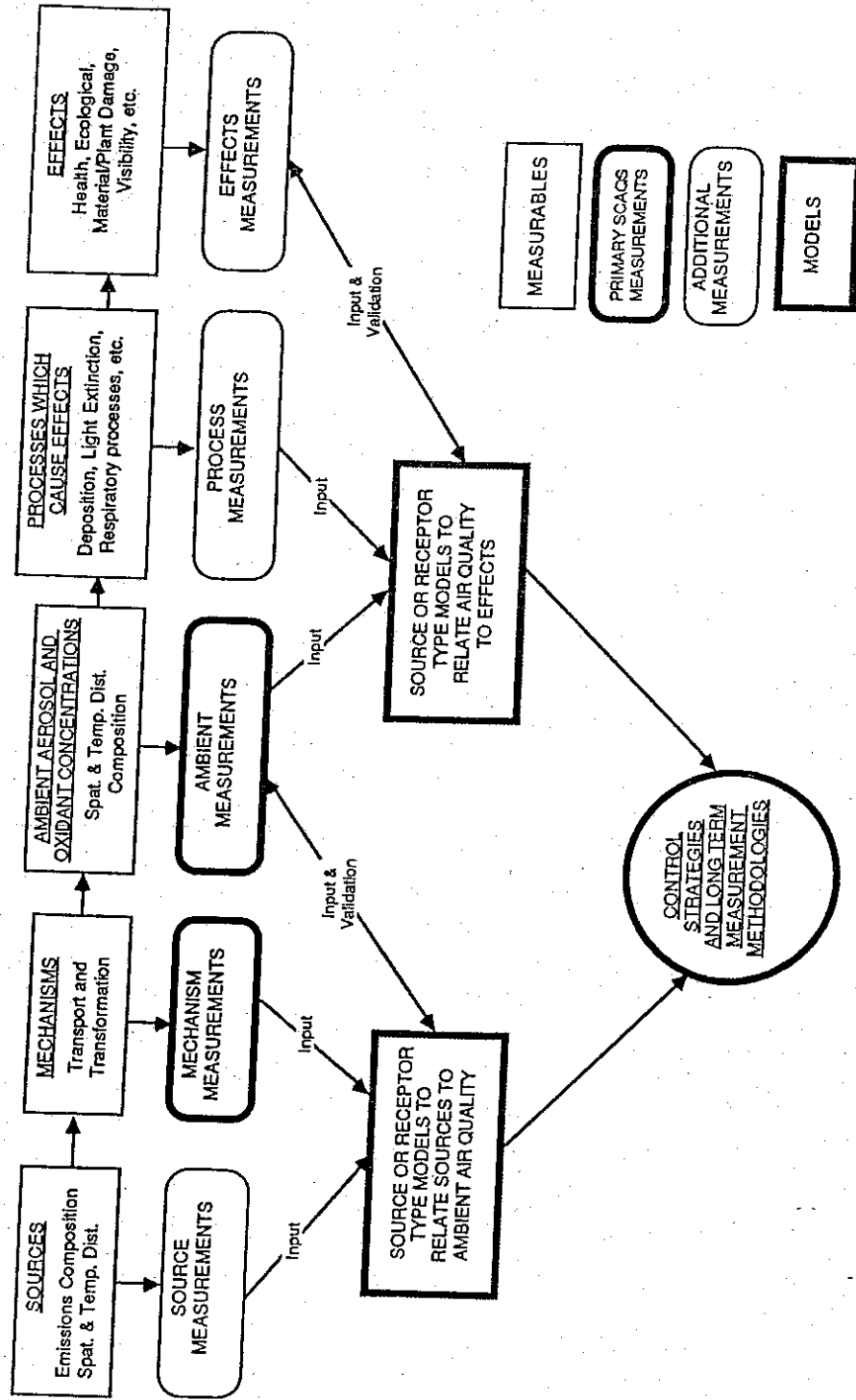


Figure 1-1. RELATIONSHIP BETWEEN MEASUREMENTS, MODELS AND CONTROL STRATEGIES

determine the relationship between the hydrocarbon/NO<sub>x</sub> ratios in ambient air and their ratios in current emissions inventories;

determine the organic composition of selected samples of source and receptor region aerosols;

determine the contribution of trace metals to atmospheric aerosols in source and receptor areas as a function of size; and

determine the spatial distribution of nitrogen species. Perform a nitrogen mass balance across the Basin, accounting for total nitrogen species through transformations and deposition.

## Objective 2

Identify the characteristics of emissions from specific sources or source types for use in receptor modeling of both gases and aerosols with emphasis on sources of organic and toxic emissions.

### Issues to be addressed:

Determine which chemical and physical properties of source emissions are most useful for source attribution of receptor concentrations.

Estimate the changes in the ratios of chemical species as a function of source-receptor travel time, interactions with other species, and meteorological conditions.

Quantify the uncertainty of source attribution by receptor models as a function of the chemical and physical properties used to characterize sources. Select the optimal properties for routine source profile measurements.

Determine the percentages of the PM-10 and fine particles which are primary and secondary. Assess the relative contributions of natural and anthropogenic sources to PM-10 concentrations.

## Objective 3

Assess the dependence of particle and O<sub>3</sub> formation and removal mechanisms upon selected meteorological and precursor variables.

### Issues to be addressed:

Assess the importance of water in the vapor and liquid phases for the formation of aerosol in the SOCAB.

Assess the role of aromatic hydrocarbons in the formation of particles and as an ozone precursor.

Assess the formation rates of nitric acid and aerosol nitrate as a function of: (1) the presence of liquid water, (2) altitude, (3) UV intensity, and (4) the presence of O<sub>3</sub>.

Determine the concentration of particulate organic matter in source and receptor areas as a function of particle size and ambient temperature. Assess the change in mass as a function of particle size, ambient temperature, and ambient pressure when particles are collected on substrates for subsequent laboratory analyses.

Determine the relationship between measurement values obtained at a single station and volume-averages over grid sizes used in prognostic air quality models.

Compare and evaluate various methods for the measurement of nitric acid and other nitrogen species and determine their accuracy, precision, and validity under a range of environmental conditions.

Compare and evaluate various methods for the measurement of carbonaceous species, and determine their accuracy, precision, and validity under a number of environmental conditions.

### 1.3.2 Modeling Considerations

The input and testing data required by air quality models were quantitatively assessed by a Model Working Group (MWG) as part of the program planning process (Seinfeld et al., 1986, 1987). The expected objectives of future modeling efforts include the following:

#### Sensitivity Testing

Performing model sensitivity tests to identify the sensitivity of model results to uncertainties in the model input data obtained during SCAQS.

#### Model Mechanisms Evaluation

Evaluating the physical and chemical bases for air quality models which describe photochemical and aerosol processes in the SOGAB.

#### Issues to be addressed:

Evaluate objective and fundamental methods of estimating three-dimensional wind fields.

Evaluate chemical and physical mechanisms for  $O_3$  and aerosol formation.

Quantify the uncertainties in model results which are caused by: (1) measurement uncertainties of the model input data and parameters, (2) deviations from model assumptions, and (3) the stochastic nature of the atmosphere.

Compare the ability of alternative mathematical models to represent atmospheric and chemical mechanisms.

(Hering and Lawson et al., 1986b and Hering et al., 1987). The results from these studies have been incorporated into the SCAQS measurement program.

The SCAQS field measurement program will take place during early to mid summer and late fall periods. During each study period, several two-day to three-day periods will be studied intensively, for a total of 18 intensive study days.

The field study will include the following elements:

- a network of existing routine air quality monitoring stations (C-sites);
- nine monitoring stations located along typical air trajectories which will measure aerosols and gases routinely on intensive study days (B-sites). B-sites will be collocated with C-sites. B-site measurements will be made by techniques of known precision and accuracy. B-site measurements will be more extensive and have better time resolution than C-site measurements. Nine B-sites will be operated in the summer period and five during the fall period;
- one research station each in a source and receptor region in the summer and one station in a source region in the fall (A-sites). These stations will be collocated with B-sites and will be the base of operations for cooperating investigators. A-site measurements will be more sophisticated and experimental than the B-site measurements;
- a network of meteorological measurements at the surface and aloft to be operated on intensive study days;
- routine upper-air pollutant and LIDAR measurements to be made by aircraft on intensive study days;
- complementary measurements of selected toxic air contaminants to be made at selected sites;
- complementary physical and chemical measurements of fog and clouds on intensive study days;
- "special" studies on selected intensive study days - including multiple tracer studies;
- assembly and archiving of complementary data from existing data sources; and
- a quality assurance program including independent systems and performance audits.

The study consists of a number of closely coordinated projects funded by several co-sponsors including the ARB, the Environmental Protection Agency (EPA), the South Coast Air Quality Management District (SCAQMD), the Coordinating Research Council (CRC), the Electric Power Research Institute

## 2. CURRENT KNOWLEDGE AND INFORMATION NEEDS

### 2.1 AIR QUALITY MANAGEMENT PLAN

The South Coast Air Basin (SOCAB) comprises 6600 square miles of the non-desert portions of Los Angeles, San Bernardino, Riverside and Orange Counties. Its population of approximately 10.5 million inhabitants is expected to increase to 13 million by the year 2000. This will be accompanied by a 31% increase in the number of dwellings and a 33% increase in employment. It is expected that 10.1 million on-road vehicles in the Basin will travel 234.3 million miles per day by the year 2000 (SCAQMD, 1982). The tremendous growth predicted over the next two decades adds to the even more rapid growth which has occurred since 1950. This growth has been accompanied by deterioration of air quality. Without careful planning and appropriate emissions controls, air quality could become even worse in the future.

The South Coast Air Quality Management District (SCAQMD) is charged with the responsibility for determining compliance with California state and federal air quality standards, proposing plans to attain those standards when they are exceeded, and for implementing those plans to the greatest extent possible. To these ends, the SCAQMD operates a network of sampling sites, illustrated in Figure 2-1, which measure ambient concentrations of carbon monoxide (CO), ozone (O<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), total suspended particulate (TSP) matter, PM-10, and suspended particulate lead. Table 2-1 presents the federal primary and secondary and California state standards for different atmospheric pollutants along with the number of sites and number of days in 1982 which exceeded these standards (Hoggan et al., 1983). Recent data for 1983 (ARB, 1983, and Hoggan et al., 1984) and earlier years are consistent with the number of exceedance cases indicated in Table 2-1. It is evident that the South Coast Air Basin was in violation of every standard, except that for SO<sub>2</sub>, at nearly every one of its sampling sites during 1982. Results for 1983, 1984, 1985 are similar and pollution levels in subsequent years are not expected to change significantly without changes in emissions. There is an obvious need to undertake measures to reduce ambient concentrations of carbon monoxide, nitrogen dioxide, ozone, and suspended particulate matter.

The most recent Air Quality Maintenance Plan (AQMP) (SCAQMD, 1982) proposes several control measures which would be implemented between now and the year 2000. SCAQMD (1982) estimates that these "Short Range Control Tactics" will cost approximately \$800 million to implement, most of which will be borne by petroleum refineries, electric utilities, and motor vehicle manufacturers. The emissions reductions are in addition to control measures which had been mandated prior to the Plan. The largest emission reductions by the year 2000 proposed in this plan result from the following additional control measures:

- Major CO reductions will result from more frequent tuneups to manufacturers' specifications; low emission, high fuel economy vehicles for local government; increased bicycling; ride sharing; modified work schedules; home goods delivery; traffic signal synchronization; electric, methanol-powered and dual-fueled vehicles; and more stringent emissions controls on in-use and new vehicles.

Table 2-1. Federal and California State Standards with Number of Sites (d) Exceeding them in 1992.

Pollutant	Federal Primary Standard	No. of Sites in Violation	Range in No. of Violation Days per site (e)	Federal Secondary Standard	No. of Sites in Violation	Range in No. of Violation Days per site (e)	California State Standard	No. of Sites in Violation	Range in No. of Violation Days per site (e)
Ozone	0.12 ppm (1 hr)	32	1 to 121	0.12 ppm (1 hr)	32	1 to 121	0.10 ppm (1 hr) (a)	33	2 to 160
Carbon Monoxide	9.0 ppm (8 hr) 35.0 ppm (1 hr)	13 0	2 to 50 0	9.0 ppm (8 hr) 35.0 ppm (1 hr)	13 0	2 to 50 0	9.0 ppm (8 hr) 20.0 ppm (1 hr)	13 6	2 to 47 1 to 7
Nitrogen Dioxide	0.05 ppm (aaa) (f) --	9 --	NA (c) --	0.05 ppm (aaa) --	9 --	NA --	--	--	--
Sulfur Dioxide	0.03 ppm (aaa) 0.14 ppm (24 hr)	0 0	0 0	0.03 ppm (aaa) --	0 --	0 --	0.25 ppm (1 hr) --	11	1 to 8
Sulfate	--	--	--	--	--	--	0.05 ppm (24 hr)	--	--
Lead	1.5 $\mu\text{g}/\text{m}^3$ (calendar qtr.)	1 (b)	1 (b)	1.5 $\mu\text{g}/\text{m}^3$ (calendar qtr.)	1 (b)	1 (b)	25 $\mu\text{g}/\text{m}^3$ (24 hr) 1.5 $\mu\text{g}/\text{m}^3$ (per 30 days)	14 2 (b)	1 to 3 1 to 3 (b)
TSP	75 $\mu\text{g}/\text{m}^3$ (aga) (g) 260 $\mu\text{g}/\text{m}^3$ (24 hr)	14 4	NA 1 to 2	50 $\mu\text{g}/\text{m}^3$ (aga) 150 $\mu\text{g}/\text{m}^3$ (24 hr)	18 23	NA 1 to 22	60 $\mu\text{g}/\text{m}^3$ (aga) 100 $\mu\text{g}/\text{m}^3$ (24 hr)	18 26	NA 2 to 37
PM-10	50 $\mu\text{g}/\text{m}^3$ (aaa) 150 $\mu\text{g}/\text{m}^3$ (24 hr)	-- --	-- --	-- --	-- --	-- --	30 $\mu\text{g}/\text{m}^3$ (aga) 50 $\mu\text{g}/\text{m}^3$ (24 hr)	-- --	-- --

(a) Oxidant instead of ozone

(b) Number of quarters instead of number of days

(c) NA - not applicable for annual average

(d) Out of a total of 35 sites for O<sub>3</sub>, 27 sites for CO, 24 sites for NO<sub>2</sub>, 21 sites for SO<sub>2</sub>, and 27 sites for TSP, lead, and sulfate.

(e) Only sites exceeding the standard at least once are included.

(f) aaa = annual arithmetic average

(g) aga = annual geometric average



### 2.2.1 Emissions

Table 2-2 presents the SOCAB emissions classified into six categories as compiled from the 1983 emissions inventory (ARB, 1986). Total emissions from the state of California are given for comparison. The emissions in several of these categories have changed since the 1979 inventory as the result of the implementation of controls on various sources and fuel switching (from oil to natural gas) in the utility industry.

The first observation from this table is that the SOCAB contained a large fraction of all emissions in the state during 1983, ranging from 26% to 38%. Furthermore, this large fraction of total state emissions was confined to only 4% of the state's land area and is roughly comparable with the area's 44% of the state population. The largest emitters of both reactive organic gases (ROG) and nitrogen oxides in 1983 were on-road vehicles. Light duty passenger vehicles and light and medium duty trucks were the largest contributors within this source category, though heavy duty diesel trucks were significant  $\text{NO}_x$  emitters. Solvent use was a major emitter of reactive organic gases, with architectural coatings, other surface coatings, and domestic uses being its major sources. Fuel combustion was also a major  $\text{NO}_x$  emitter, with the electric utilities being the highest contributor within this category. The large total organic gas (TOG) emission rate derived largely from solid waste landfills. Tilling, re-suspended road dust, and light-duty passenger vehicle emissions were the major primary particle emitters, with diesel trucks and mineral processing also of significance.

There are slight seasonal deviations in these Basin-wide emission rates; these changes are typically within the measurement uncertainty of the inventory process (Grisinger et al., 1982). Seasonal differences are related primarily to weather conditions, with higher fuel consumption in the wintertime for heating. Reactive organic emissions are higher in the summer owing to the use of paints in construction. The increased CO and particle emissions from fuel combustion in the winter are somewhat offset by negligible winter emissions from the unplanned fires which take place intermittently during the hot summer months. Thus, while the aggregate emission rates do not vary appreciably over the year, the temporal and spatial detail of these emissions varies significantly. Figures 2-2 and 2-3 show the gridded emissions of TOG, CO,  $\text{NO}_x$ ,  $\text{SO}_x$ , and TSP from surface and elevated point sources. These figures illustrate the spatial complexity of emissions in the SOCAB. They represent 1982 emissions projections from 1979 data. The vertical scales of each figure are unequal, so comparisons among Figure 2-2, Figure 2-3, and Table 2-2 must be qualitative. Nevertheless, several inferences can be made. Surface emissions of TOG, CO, and  $\text{NO}_x$  have similar spatial distributions. These emissions are highest near the center of the Basin and taper off near the coastal areas and toward the eastern extremes. Table 2-2 implies that the major sources of these species are on-road vehicles. Surface  $\text{SO}_x$  emissions are most concentrated near and southeast of the Palos Verdes peninsula. Table 2-2 implies that petroleum transfer and storage and low-level combustion of sulfur-containing fuels take place in these grid squares. Surface particulate emissions are more uniformly distributed throughout the Basin with several large peaks which are probably attributable to some of the "miscellaneous processes" listed in Table 2-2. The downtown particle peak corresponds to similar patterns on the TOG, CO, and  $\text{NO}_x$  plots and can probably be attributed

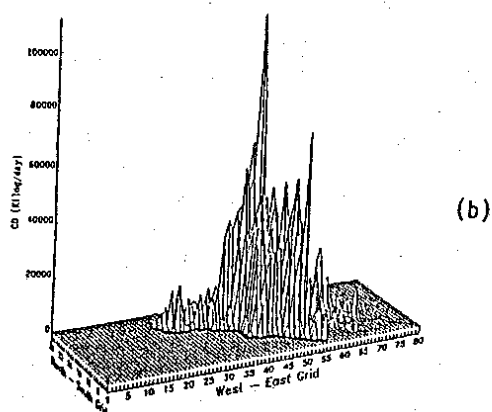
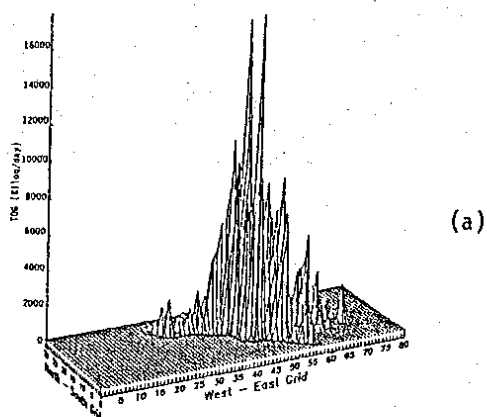


Figure 2-2. Spatial Pattern of Surface Emissions (<10 m AGL) in the South Coast Air Basin. These Data are 1982 Projections from the 1979 Emission Inventory for TOG (a), CO (b), NO<sub>x</sub> (c), SO<sub>x</sub> (d), and TSP (e) (personal communication with Ed Yotter of ARB, (1986).

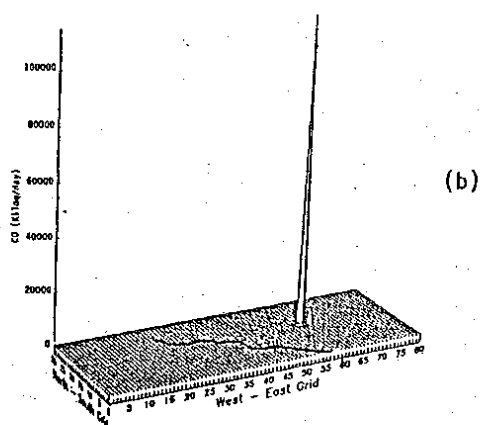
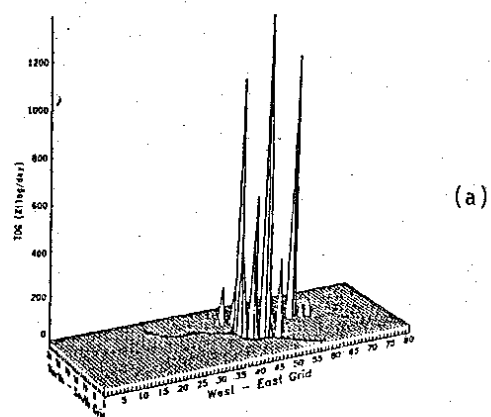


Figure 2-3. Spatial Pattern of Elevated Emissions (>10 m AGL) in the South Coast Air Basin. These Data are 1982 Projections from the 1979 Emission Inventory for TOG (a), CO (b), NO<sub>x</sub> (c), SO<sub>x</sub> (d), and TSP (e) (personal communication with Ed Yotter of ARB, 1986).

to re-suspended road dust. The east Basin peaks could be attributable to agricultural tilling.

The peaks for all pollutant emissions in Figure 2-3 originate from the same point sources, and they are relatively few. Grisinger et al. (1982) list these sources and their location in order of emission rate. These elevated emitters are concentrated along the middle and southern coast with a few located in the east Basin.  $\text{NO}_x$  appears to be the most widely distributed elevated source, and many of its isolated appearances probably result from natural gas combustion which is accompanied by few other pollutant emissions. The elevated emissions of suspended particulate matter are more isolated in space than are the surface emissions, but their emissions rates are comparable to or greater than the surface rates in corresponding grid squares.

The temporal variations in pollutant emissions are not well documented. Though Grisinger et al. (1982) provide diurnal patterns for on-road vehicle emissions which show peaks during the morning and evening rush hours and lower than average emissions at night, these patterns are inferred rather than measured. SCAQMD receives daily  $\text{NO}_x$  emission rates from large stationary sources, but these are not formally incorporated into the inventory process. The ambient concentration changes observed during the 1984 Olympics by Davidson and Cassmassi (1985) indicate that temporal emission distributions may have an important effect on the products of those emissions.

The ARB and SCAQMD emissions inventory for the South Coast Air Basin is one of the best of its type in existence. Nevertheless, it contains uncertainties which derive from errors in the vast amount of acquired data, emission factors which are not derived from the specific emissions sources, and variable or undocumented process rates. The emission rates reported in Table 2-2 reflect activities as they were in 1983. Even though SCAQMD (1982) has made projections into 1987, these projections are no substitute for a re-assessment of the emitting sources during the year of concern.

The 1983 inventory may not even present an entirely accurate picture for that year. Emission rates from stationary sources which exceed 10 tons/year are updated with each inventory revision from approximately 65,000 permits filed by 10,000 companies. Emissions from smaller sources are not routinely re-estimated, and these can account for more than 50% of the reactive organic gas emissions from stationary sources. Biogenic and geogenic emissions are not included in the inventory, and these could be significant.

Grisinger et al. (1982) provide semi-quantitative estimates of the uncertainty of emission rates for the 1979 inventory, and the Basin-wide estimates recorded in Table 2-2 are tolerable for most assessment purposes. The individual emissions category uncertainties, however, range from 15% to 100% (these coefficients of variation are one standard deviation centered on the average emission rate estimate). Uncertainties for ROG rates from major emission categories such as surface coatings and gasoline hot soak and evaporation are especially large (30% to 40%). Uncertainties associated with smaller spatial scales and time intervals probably are much higher than these estimates.

One specific concern involves the uncertainty of the ratio of reactive hydrocarbons to nitrogen oxides ( $\text{NO}_x$ ) emissions which is used in the EKMA

mostly during winter. Frequent and persistent temperature inversions are caused by subsidence of descending air warmed by compression settling over the cool, moist marine air. These inversions often occur during periods of maximum solar radiation (SCAQMD, 1982). Relative humidities can vary, depending on the origin of the air mass. RH typically exceeds 50% throughout the basin, being higher near the coast than farther inland (Smith et al., 1984).

As illustrated in Figure 2-1, the SOCAB is surrounded on the north, east, and west by mountains, some of which rise above 10,000 feet. The Basin opens to the Pacific Ocean on the southwest. The topography of the Basin combined with the land/sea interface introduces important mesoscale effects which are superimposed on the synoptic weather patterns.

Figures 2-4 and 2-5 from Smith et al. (1972) illustrate the diurnal evolution of surface flow patterns in the SOCAB for summer and winter months respectively. Similar patterns were found by Keith and Selik (1977). In the summertime, the sea breeze is strong during the day and there is a weak land-mountain breeze at night. Because of the high summer temperatures, the land temperature does not usually fall below the water temperature at night, and the nocturnal winds are slow and weak. The opposite is true during the winter, when the mountain-land breeze at night yields strong ventilation, and a mild sea breeze is only established late in the day when temperatures approach their maxima.

The predominant trajectories are from the west and south during summer mornings, switching to predominantly westerly flows by the late afternoon and early evening. These summertime trajectories become difficult to discern at night owing to the generally stagnant conditions. As shown in Figure 2-5, the prevailing wintertime trajectories are from the east and north at night, switching to westerly trajectories by late afternoon. In both cases, there is strong propensity for the transport of emissions from the western and southern parts of the SOCAB to the eastern and northern parts, with this propensity being higher during the summer months than in the winter months. Aircraft (e.g. Blumenthal et al., 1978; Calvert 1976a, 1976b), tetroon (e.g. Angell et al., 1976), and tracer (e.g. Shair et al., 1982) studies provide results which are qualitatively consistent with the trajectories illustrated in Figures 2-4 and 2-5.

The land/sea breeze circulation can cause air to transfer back and forth between the Basin and the Pacific Ocean. Cass and Shair (1984) estimated that up to 50% of the sulfate measured at Lennox was attributable to backwash of emissions which had been transported to sea on the previous day. During the daytime, emissions from coastal sources are advected inland by the sea breeze. At night, these polluted air masses are swept back toward the coast to await their re-entry to the Basin on the following day. There is ample evidence (e.g. Kauper and Niemann, 1975; 1977), however, that a good portion of these pollutants which pass the coastline can be transported to neighboring air basins.

Air from the Basin can exit through a number of routes other than the sea. Smith and Shair (1983) found transport routes through Soledad Canyon, Cajon Pass, and San Geronimo Pass when they released tracer gases in the South Coast Air Basin. Smith and Shair (1983) also showed evidence of transport aloft from the San Fernando Valley into eastern Ventura County. Godden and

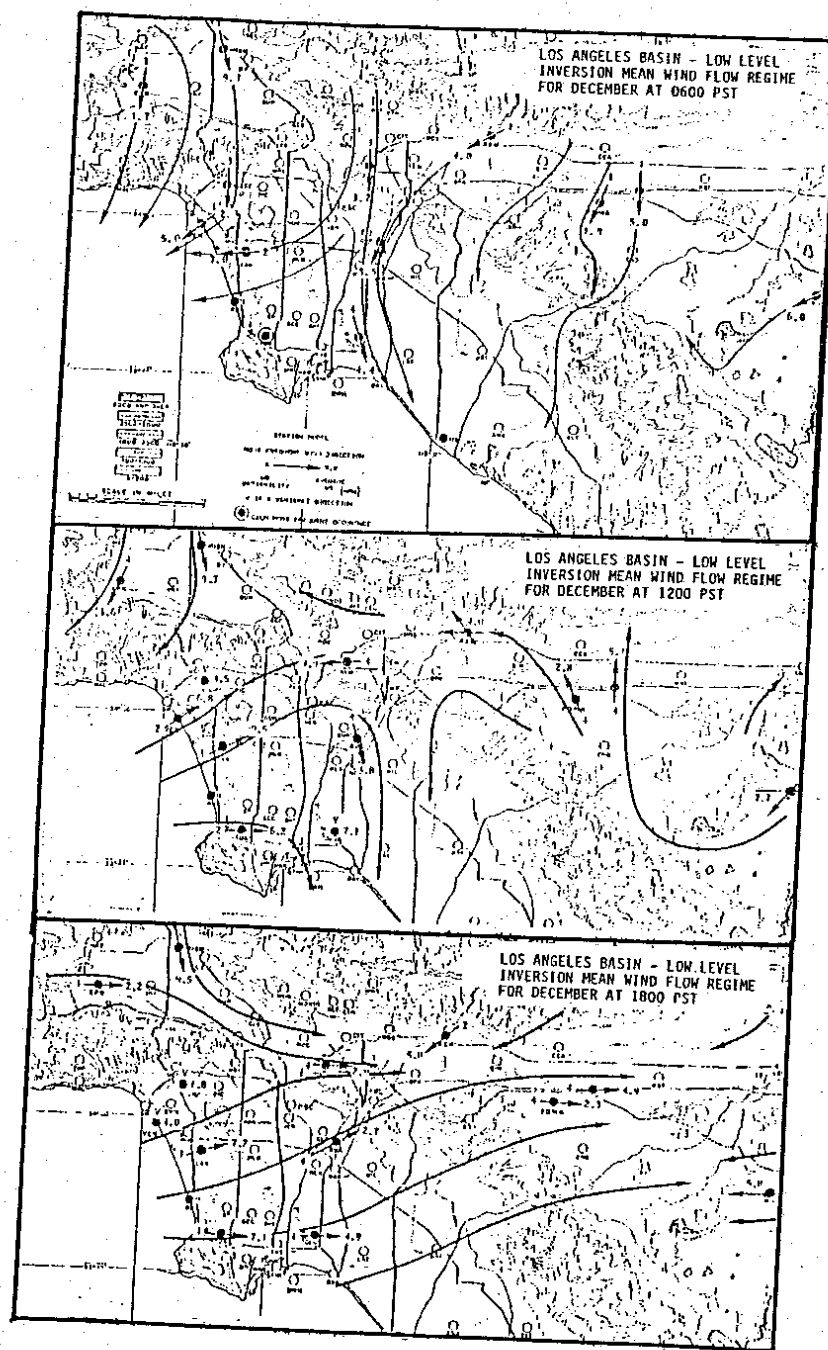


Figure 2-5. Winter Variation in Surface Wind Flow Patterns throughout the Day in the South Coast Air Basin (Smith et al., 1972).

peak of  $\text{NO}_2$ , which is in turn followed by a peak in ozone concentrations in the early to late afternoon (depending on the location of the sampling site). While these qualitative features are well-established and reproducible, the chemistry and physics describing them is not. Dunker et al. (1984), Leone and Seinfeld (1984a, 1984b), and Killus and Whitten (1983) have compared the most recent photochemical reaction mechanisms applied to similar situations. Though all mechanisms exhibit the same qualitative features of reactant and end-product concentrations with time, the peak values and the time of occurrence of those peaks are mechanism dependent. The practical mechanism which is most representative of reality is still open to judgment.

Photochemical sulfate formation in the Los Angeles atmosphere typically follows a diurnal cycle with a daytime maximum rate near 6% per hour (Roberts, 1975; Cass, 1981). Nitrogen dioxide is converted to nitric acid by hydroxyl radicals at rates five to ten times faster than sulfur dioxide is converted to sulfate (Forrest et al., 1981). Nitrogen dioxide is also converted to peroxyacetyl nitrate (PAN), and the proportions depend on the initial  $\text{ROG}/\text{NO}_x$  ratios (Spicer et al., 1983). Russell et al. (1985) found that over a 24 hour trajectory simulation, 7% of  $\text{NO}_x$  emissions were transformed to airborne  $\text{HNO}_3$ . Though both nitric acid and PAN are gases, nitric acid is also present in liquid particles. The photochemical formation of organic aerosol is less well understood (Pitts et al., 1978; Hidy and Mueller, 1979), but is the subject of much current work. Studies of organic aerosol formation are inconclusive because of the plethora of precursors and the volatilities of their products. Theoretical mechanisms for the photochemical conversion of gases to particles are still in their formative stages.

The differences between inventoried and ambient  $\text{ROG}/\text{NO}_x$  ratios can be explained, at least in part, by these theoretical reaction mechanisms. Haney and Seigneur (1985) re-examined the ambient  $\text{ROG}$  and  $\text{NO}_x$  concentrations generated by a recent application of the SAI urban airshed model to the SOCAB which used an initial  $\text{ROG}/\text{NO}_x$  emissions ratio of 2.86. They found that the  $\text{ROG}/\text{NO}_x$  ratios at Anaheim and Downtown L.A. reached values of 7 to 9 during the hours just past noon and dropped to values of 3 to 5 at night. The afternoon values correspond to the period of maximum ozone production, when a large portion of the ambient  $\text{NO}_x$  is reduced by photochemical reactions. Photochemistry ceases after sunset, allowing the  $\text{NO}_x$  to be replenished. Calculations for Riverside show ratios ranging from 4.5 to 61.7 because the pollutants have undergone longer photochemical reaction times and ambient  $\text{NO}_x$  levels are much lower than those at the downtown sites. Haney and Seigneur (1985) conclude that the faster oxidation of  $\text{NO}_x$  with respect to  $\text{ROG}$  during photochemical smog formation can account for the difference between inventoried and ambient  $\text{ROG}/\text{NO}_x$  ratios and that neither the inventory nor the ambient measurements are necessarily in error.

Though photochemical transformation processes are of greatest importance for the production of ozone, gases can be transformed into suspended particulate matter by a number of other processes. Husar et al. (1976) show direct evidence of the condensation of gaseous species on solid or liquid particles. Relative humidity changes affect the water content of aerosols, which have consequences with respect to their size and their propensity to scatter light (Charlson et al., 1969; Covert et al., 1972; Tang et al., 1981). This effect tends to be important at relative humidities above 70% when many dry, ionic particles deliquesce. Sulfate formation rates increase when small

determining ozone standard violations. They found that as few as ten of the SCAQMD stations would provide an accurate estimate of the number of exceedances per site. The coverage of this network is such that coastal, inland, and valley areas are represented. All EPA siting criteria and shelter requirements are complied with at all sites.

Table 2-3 identifies the routine measurements which are made at existing sampling sites in the South Coast Air Basin. Carbon monoxide by non-dispersive infrared spectrophotometry, ozone by ultraviolet photometry, nitric oxide and nitrogen oxides by chemiluminescence, sulfur dioxide by pulsed fluorescence, total hydrocarbons by flame ionization detector, and total suspended particulate matter by standard HiVol samplers are measured at most sites. Gas concentrations of one-hour duration are acquired continuously and suspended particle samples of 24-hour duration are acquired on an every-sixth-day schedule. Mass, sulfate, nitrate, and lead measurements are made on most of the HiVol samples. Size-classified particulate matter in the 0 to 10  $\mu\text{m}$  size range is currently being collected at 11 sites, as indicated in Table 2-3, using automatic mass flow controlled high volume samplers with Sierra-Anderson 321A size-selective inlets. This monitoring is being performed in anticipation of the promulgation of a new national ambient air quality standard for particulate matter (Federal Register, 1984) and to determine compliance with California's size-selective particulate matter standard. Mass, sulfate and nitrate measurements are currently being made on these samples.

Table 2-3 also shows the distribution of surface meteorological monitoring networks which acquire wind speed, wind direction, temperature, relative humidity, and insolation data. Goodin et al. (1979, 1980) have examined the adequacy of this network for replicating a known surface wind field and have found it adequate when the proper interpolation and adjustment schemes are used. The network is not adequate, however, for determining a three-dimensional wind field.

Ambient air quality data acquired from this network over many years show the following general features taken from the 1982 Summary of Air Quality (SCAQMD, 1983; Hoggan et al., 1983):

- Ozone. Coastal stations experience the lowest concentrations and the lowest number of standard exceedance cases. Concentrations increase sharply from the coastal to the inland valley portions of the Basin. The area with the highest ozone levels extends from the San Fernando Valley through the San Gabriel Valley and into the Riverside-San Bernardino area and adjacent mountains. In 1982, Azusa, Pico Rivera, Los Angeles, and Norco exhibited hourly ozone concentrations in excess of 0.35 ppm. The highest value of 1982 was 0.40 ppm which occurred at the downtown Los Angeles site between noon and 1 p.m. on September 2, 1982. Figures 2-6a, b, c, and d show long-term trends, monthly averages, and the diurnal pattern of ozone concentrations at Azusa which are typical of the patterns at most inland sites in the network. Highest ozone dosages tend to occur at elevated sites in the San Gabriel and San Bernardino Mountains. NO values are very low at these sites, and there is little opportunity for the  $\text{O}_3$  which reaches them to be scavenged.
- Carbon Monoxide. More than half of the SOCAB stations are in compliance with the CO standard. The highest concentrations are observed during the



Table 2-3. (continued)

Site Code	Sampling Site	Pollutants Monitored										Meteorological Measurements		
		O3	NO/NOx	Gaseous CO	SO2	THC(a) NMHC (b)	TSP	Pb	SO4	HTVol NO3	TOF (c) PM10	Temp	Humidity	WS/WD (d) Radiation
44	San Bernardino	X	X	X	X		X	X	X	X				X
45	San Juan													
46	Capistrano													X
47	Santa Monica AP													X
48	Torrance AP	X	X	X	X	X	X	X	X	X		X	X	X
49	Upland													X
50	Van Nuys													X
51	Venice													X
52	W. LA	X	X	X	X	X	X	X	X	X				X
53	Whittier	X	X	X	X	X	X	X	X	X				X
54	Zuma Beach													X
55	Beaumont													X
56	Fullerton AP											X	X	X
57	Mt. Wilson											X	X	X
58	Pomona AP													X
UPPER AIR														
25	Loyola-													
33	Marlymount													
	Ontario AP	X										X	X	X

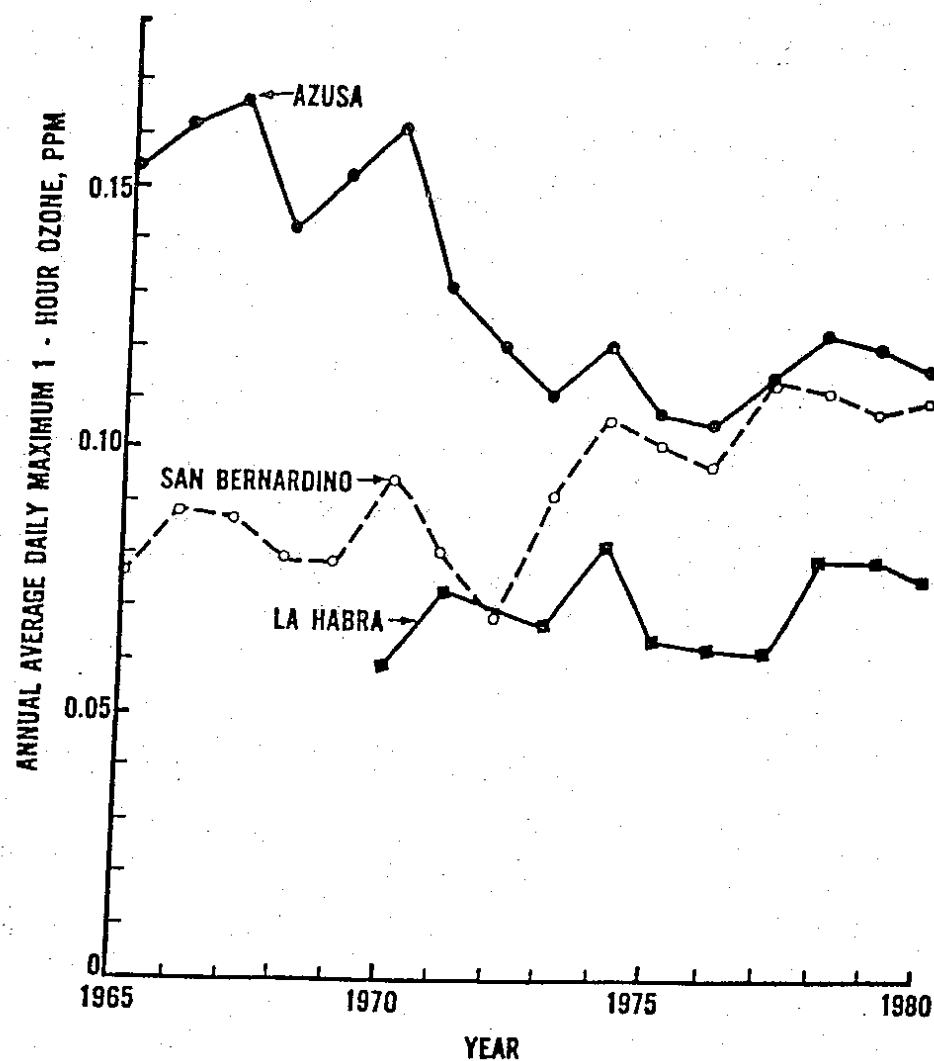


Figure 2-6a. Sixteen Year Trend in the Annual Average of Daily Maximum 1-Hour Ozone Concentration from 1965 to 1980 at Azusa, San Bernardino, and La Habra. (SCAQMD, 1981)

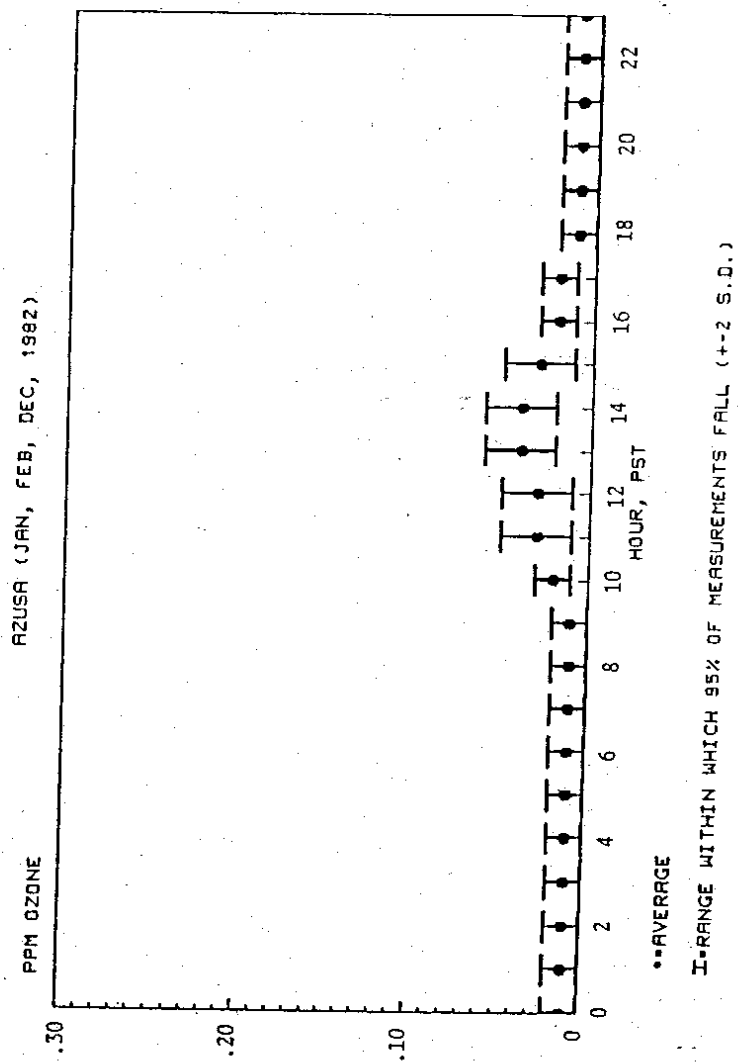


Figure 2-6c. 1982 Winter Average Ozone for Each Hour at Azusa, CA. (Hoggan et al., 1983)

winter at Lennox, Lynwood, Burbank, and Reseda. The highest one-hour value of 27 ppm in 1982 occurred at Lynwood on December 17, 1982. The diurnal distribution of CO follows the morning and evening rush hours. This pollutant is particularly useful in identifying the presence or absence of motor vehicle emissions at each receptor.

- Sulfur Dioxide. SO<sub>2</sub> concentrations are generally low throughout the Basin, except when the monitor encounters a plume. Daytime concentrations are generally higher than nighttime concentrations. This is consistent with SO<sub>2</sub> emissions from elevated sources being injected above the nighttime mixing layer. For the most part, the presence of this pollutant indicates the influence of nearby elevated source emissions. The maximum twenty-four hour average SO<sub>2</sub> concentration in 1982 was 36 ppb at Lennox on December 7.
- Nitrogen Oxides. Highest concentrations were found in 1982 at Los Angeles, West Los Angeles, Lennox, Long Beach, and Whittier. NO<sub>2</sub> concentrations do not show consistent patterns across the Basin, probably owing to the multitude of possible interactions of this pollutant with other pollutants, nearby emissions, and meteorological variables. The maximum hourly average NO<sub>2</sub> concentration in 1982 was 410 ppb measured at Los Angeles on September 3. This followed closely on the maximum ozone concentration which was measured at the same site on the preceding day.
- Total Suspended Particulate Matter. The highest 24 hour TSP levels are detected in an area extending from the eastern San Gabriel Valley, through the Pomona Valley and into the Riverside-San Bernardino area. Seasonal averages vary from location to location, indicating the multiplicity of factors affecting TSP concentrations. The sulfate, nitrate, and lead fractions of TSP provide some insight into the contributors to these pollutant levels. Sulfate typically comprises 7%-13% of TSP and the highest levels are consistently found downwind of major SO<sub>2</sub> emission sources. Highest sulfate levels generally occur during the late summer under conditions of high humidity, while the lowest concentrations are evident in the winter. Nitrate typically comprises 12%-20% of TSP. Highest levels are experienced in the San Bernardino - Riverside area in the summer and fall. Lead concentrations ranged from 0.3% to 1.1% of TSP in 1982 and are decreasing as lead is phased out of use in the motor vehicle fleet (Hoggan et al., 1978). Highest lead levels in 1982 were found in the densely populated areas of Lennox and Lynwood. In 1982, the highest TSP value of 272 µg/m<sup>3</sup> occurred at Fontana on July 16 and the highest daily sulfate value of 37.3 µg/m<sup>3</sup> occurred at Lennox on December 7, though most other high values were found in the September/October time-frame. The highest annual average nitrate of 21.3 µg/m<sup>3</sup> occurred at Riverside and the highest monthly average lead level was 1.7 µg/m<sup>3</sup> at Lennox in October. SCAQMD has estimated PM-10 annual averages from 1984 TSP data (Figure 2-7). These averages are likely to exceed 50 µg/m<sup>3</sup> at nearly all SOCAB sampling sites, with the sites in the San Bernardino/Riverside areas having the highest values. Measured PM-10 values at seven sites show that Downtown L.A., Rubidoux, Azusa, Burbank, Long Beach and Los Alamitos exceed the new annual PM-10 standard. Only Rubidoux exceeded the new 24 hr PM-10 standard of 150 µg/m<sup>3</sup> with a high concentration of 208 µg/m<sup>3</sup>.

While most historical monitoring has focused on  $O_3$ ,  $CO$ ,  $SO_2$ ,  $NO_2$ , and TSP owing to their regulation by National Ambient Air Quality Standards, it has been recognized that particulate and gaseous organic material, nitrogenous substances, trace metals, atmospheric mutagens, acid deposition, and visibility are also phenomena of public concern. Both short-term and long-term monitoring programs have been implemented to study these issues. Typical concentrations and ranges for several of these measurements are summarized in Section 3.

A major concern in the interpretation of receptor measurements has been the extent to which these measurements are representative of actual concentrations in the atmosphere. The limitations of measurement technology have repeatedly clouded the interpretation of data used to elucidate cause and effect relationships between variables.

Oxidant measurements taken in the SOCAB prior to 1974 indicated that the major problem areas were confined to the eastern cities in the Basin, and scrutiny of mid-Basin cities, such as Pasadena, was minimized. Pitts et al. (1976) reexamined the oxidant measurements taken between 1955 and 1974 after applying corrections for different calibrations (buffered and unbuffered KI calibrations were converted to an ultraviolet absorption standard) used in Los Angeles County and other counties of the SOCAB. Their re-interpretation of the corrected data concluded that "...oxidant levels do not increase along a west to east axis across the basin [as was previously believed]....they do increase along a southwest to northeast axis across the basin, which roughly matches the orientation of the prevailing onshore sea breezes." Hydrocarbon interferences with the current ultraviolet absorption ozone measurement method must be considered in interpretation of ozone measurements derived from it.

Winer et al. (1974) have quantified the interference of PAN and several other organic nitrates in the chemiluminescent monitoring of  $NO_2$ . Nitroethane and nitric acid were found to interfere, but only semi-quantitative estimates are given by Winer et al. (1974). Grosjean (1983) observed that "On smoggy days... $NO_2$  can be seriously overestimated if the response of chemiluminescent instruments to PAN and HONO is not taken into account." He found that  $NO_2$  was overestimated by as much as 33%, 56%, and 65% in three different smog episodes. Godden and Lurmann (1983) found that many of their model predictions of  $NO$  and  $NO_2$  could easily fall within the range of uncertainties caused by the unknown degree of measurement interference caused by other nitrogenous species. These measurement interferences clearly affect the interpretation of these data and the determination of compliance with standards.

The particle size ranges and chemical composition of routine TSP measurements have been shown to be uncertain. The standard HiVol sampler has a 50% sampling effectiveness between 30 and 50  $\mu m$ , depending on wind speed and sampler orientation with respect to the wind direction (McFarland et al., 1979). The glass fiber filters used for SOCAB measurements in the recent past yielded higher sulfate and nitrate concentrations than were actually present in the atmosphere (Witz and MacPhee, 1977; Witz and Wendt, 1981; Witz et al., 1982). Spicer (1977) warns that "...some of the extreme particulate nitrate levels recorded in Southern California [in ACHEX] during 1-2 hr afternoon sampling periods may be attributable in part to collection of artifact nitrate." Grosjean (1975) found that the benzene-soluble organic fraction of TSP, which has been measured for years on SOCAB samples, is a variable

Table 2-4. Previous Air Quality Related Studies Undertaken in the South Coast Air Basin

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EMISSIONS INVENTORY AND CHARACTERIZATION:

ARB (1986)  
 Cass et al. (1982a)  
 Chass and George (1960)  
 Dzuby et al. (1979)  
 Grisinger et al. (1982)  
 Huang and Head (1978)  
 Mayrsohn and Crabtree (1976)  
 Mayrsohn et al. (1977)  
 Oliver and Peoples (1985)  
 Parungo et al. (1980)  
 Pitts et al. (1984)  
 Poeschel et al. (1979)  
 Richards et al. (1976, 1977)  
 Rodas and Holland (1981)  
 Rose et al. (1965)  
 Taback et al. (1979)  
 Tombach (1982)

METEOROLOGY, WIND FIELDS AND DISPERSION:

Ackerman (1977)  
 Angell et al. (1975, 1976)  
 Blumenthal et al. (1978, 1979)  
 Cass and Shair (1984)  
 Chang and Norbeck (1983)  
 Crane et al. (1977)  
 Drivas and Shair (1974a, 1974b)  
 Drivas (1975, 1982)  
 Edinger (1959)  
 Edinger and Helvey (1961)  
 Edinger et al. (1972)  
 Farber et al. (1982b)  
 Gloria et al. (1974)  
 Goodin et al. (1979)  
 Goodin and Lague (1983)  
 Hanna (1977)  
 Hidy et al. (1971)  
 Hinds (1970)  
 Husar et al. (1977)  
 Kauper and Niemann (1975, 1977)  
 Keith and Selik (1977)  
 Lissaman (1973)  
 McElroy et al. (1982)  
 McRae et al. (1981)  
 Pack and Angell (1963)  
 Panofsky (1975)  
 Reible et al. (1982)  
 Sackinger et al. (1982)  
 Schultz and Warner (1982)

Table 2-4. (continued)

Charlson and Pierrard (1969)  
 Charlson (1972)  
 Covert et al. (1972)  
 Ensor et al. (1972)  
 Noll et al. (1968)  
 Pratsinis et al. (1984)  
 Thielke et al. (1972)  
 Thomas (1962)  
 Trijonis (1982a, 1982b)  
 White and Roberts (1977)

#### SULFATE AND NITRATE MEASUREMENTS AND RELATIONSHIPS TO SOURCES:

Appel et al. (1977a, 1977b, 1978, 1982)  
 Baboolal and Farber (1982)  
 Cass (1975, 1978b, 1981)  
 Grisinger (1982a)  
 Grosjean (1982a)  
 Harker et al. (1977)  
 Heisler et al. (1980)  
 Henry and Hidy (1979)  
 Hering and Friedlander (1982)  
 Novakov et al. (1972a, 1972b)  
 Richards (1983)  
 Roberts and Friedlander (1975)  
 Russell et al. (1983)  
 Russell (1985)  
 Russell et al. (1985)  
 White et al. (1978)  
 Witz and MacPhee (1977)  
 Witz and Wendt (1981)  
 Witz et al. (1982)  
 Zeldin et al. (1983)

#### CARBONACEOUS, ORGANIC, HYDROCARBON, AND HALOCARBON MEASUREMENTS (including toxic organics):

Altshuller and Bellar (1963)  
 Altshuller and McPherson (1963)  
 Altshuller et al. (1966)  
 Appel et al. (1976, 1977a, 1979)  
 Brenner et al. (1980)  
 Cass et al. (1982b)  
 Cronn et al. (1977)  
 Duval and Friedlander (1981)  
 Ellis et al. (1984a, 1984b)  
 Ellis and Novakov (1982)  
 Gordon et al. (1968)  
 Gordon and Bryan (1973)  
 Gordon (1976)  
 Gray et al. (1985)  
 Grosjean and Friedlander (1975)  
 Grosjean et al. (1983)

Table 2-4. (continued)

Caporaletti et al. (1977)  
 Chang et al. (1980a)  
 Chock (1982, 1985)  
 Chock and Levitt (1976)  
 Chock et al. (1982)  
 Coyne and Bingham (1977)  
 Davidson and Cassmassi (1985)  
 Decker (1972)  
 Edinger et al. (1972)  
 Edinger (1973)  
 Eldon and Trijonis (1977)  
 Elkus and Wilson (1977)  
 Estoque (1968)  
 Evans (1977)  
 Farber et al. (1982a)  
 Feigley and Jeffries (1979)  
 Fontjin et al. (1970)  
 Grosjean (1982a)  
 Grosjean et al. (1983)  
 Grosjean and Fung (1984)  
 Hamming and Dickinson (1966)  
 Hanst et al. (1982)  
 Harris et al. (1982)  
 Johnson and Singh (1976)  
 Kok (1983)  
 Kopczynski et al. (1972)  
 Lawrence (1972)  
 Lea (1968)  
 Levitt and Chock (1976)  
 Lin (1982)  
 Littman et al. (1956)  
 Ludwig et al. (1981, 1983)  
 McKee (1976)  
 Merz et al. (1972)  
 Miller and Ahrens (1970)  
 Mosher et al. (1970)  
 Paskind and Kinoshita (1974)  
 Phadke et al. (1977)  
 Pitts et al. (1976)  
 Platt et al. (1980)  
 Renzetti and Romanovsky (1956)  
 Reviett (1978)  
 Rogers et al. (1956)  
 Russell et al. (1985)  
 Schuck et al. (1966)  
 Severs (1975)  
 Simmonds et al. (1974)  
 Spicer (1977)  
 Spicer et al. (1983)  
 Stephens (1968, 1969)  
 Tiao et al. (1975a, 1976)  
 Tombach (1982)  
 Trijonis and Eldon (1978)  
 Trijonis and Mortimer (1982)



Table 2-4. (continued)

Seigneur et al. (1983c)  
Tesche and Burton 1978  
Tesche et al. (1984)  
Trijonis (1972, 1974, 1983)  
Trijonis and Arledge (1975)  
Trijonis et al. (1978a)

## CARBON MONOXIDE AND PRIMARY NITROGEN DIOXIDE:

Aron and Aron (1978a, 1978b)  
Chang et al. (1980b)  
Colucci and Begeman (1969)  
Hamming et al. (1960)  
Horie and Mirabella (1982)  
Liu and Goodin (1976)  
Neuroth (1979)  
Pandolfo and Jacobs (1973)  
Pandolfo et al. (1976)  
Rogers (1958)  
Tiao et al. (1975b)  
Trijonis et al. (1975b)  
Ulbrich (1968)  
Witz and Moore (1981)  
Witz et al. (1982)

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- the multimodal aerosol size distribution was confirmed, with a submicron fraction dominated by aerosol formed from anthropogenic emissions and a supermicron fraction derived from dust and natural sources;
- sulfate, nitrate, and organic species were primarily in the submicron size range. Sulfate was more effective, per unit mass, than any other species in reducing visibility;
- the portion of aerosol attributable to photochemical processes was consistently in the 0.1 to 1.0  $\mu\text{m}$  size range;
- the photochemical mechanism was a major contributor to the formation of sulfate, nitrate, and organic particles. Heterogeneous formation pathways were also inferred to be important;
- ammonia has an important influence on the formation of photochemical aerosol, and these particles may contain a large fraction of water;
- though many sources contribute to the aerosol, sulfate is mainly linked to stationary sources using fuel oil; organic materials result from transportation using gasoline; and nitrates derive from both of these sources;
- more than half of the total suspended particulate material in the SOGAB measured during ACHEX was due to atmospheric chemical reactions. The remaining half was attributed to primary emissions from stationary and transportation sources and background materials such as sea salt and soil dust; and
- the aerosol sources and constituents primarily responsible for visibility reduction varied over the Basin, with sulfate and transportation sources being generally of greatest importance.

ACHEX was a state-of-the-art study for its time. Many of the instruments in common use today were developed for and tested in this study. Since ACHEX, much has been learned via laboratory experiments and field studies regarding the interactions of atmospheric variables, and this knowledge has been incorporated into complex and computationally intensive models which simulate these interactions. In hindsight, and with this additional knowledge, a study to address the issues raised by the above-stated conclusions would be designed quite differently from ACHEX. This hindsight does not detract from the value provided by measurements and data interpretation provided by these researchers more than a decade ago. Of particular note are the large number of publications and fundamental theories which resulted from ACHEX. These results are a direct consequence of the participation of a variety of experts, the open planning process and the free data exchange protocols established at its outset. Several subsequent air quality studies have cost more but were less influential because they neglected these important features.

The Los Angeles Reactive Pollutant Program (LARPP) consisted of airborne meteorological and pollutant sampling of coherent air parcels as they moved along a trajectory. Thirty-five days of sampling were conducted between September and November of 1973. Tetroons and tracer releases were used to locate the positions of air parcels, and instrumented helicopters continuously

Contrasting ACHEX and LARPP to the AQMP, it is evident that the research and regulatory needs are complementary. While the regulatory process must continue with the information it has, regardless of the imperfection of that information, it can nevertheless identify where more precise information is needed to make effective decisions. Research efforts can then include, and possibly even focus on, those information needs.

## 2.4 CONTEMPORARY AND FUTURE AIR QUALITY STUDIES IN THE SOCAB

There is an obvious need for further research to address the cause and effect relationships between emissions, meteorology, and ambient concentrations of precursors and products for ozone and suspended particulate matter. Knowledge of the distributions of other pollutants (such as acidic species and toxic air contaminants) and of their effects on human health, visibility, and materials, is still sparse in the SOCAB. Basic information on the values attained by these observables and their spatial and temporal distributions is needed before these important relationships can be established. The sources, emission rates, and locations of species other than particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, and ozone need to be determined. Little is known about PM-10 in the SOCAB and how it is similar to and differs from TSP. With the advent of a new PM-10 standard, and the necessity to create an implementation plan within nine months of promulgation of that standard (Federal Register, 1985), this information becomes even more topical.

Several air quality studies have recently been completed, are currently taking place, or are in the planning stages, which address measurement and modeling issues which are relevant to SCAQS. Some of these have been used in the design of, or made an integral part of, SCAQS.

- The ARB is currently taking samples of benzene, carbon tetrachloride, chloroform, ethylene dibromide, ethylene dichloride, methyl chloroform, perchloroethylene and trichloroethylene gases in Tedlar bags for gas chromatographic analysis. HiVol samples are also being taken with total chromium, lead, manganese and nickel being measured by X-ray fluorescence. The state-wide network includes the Los Angeles, El Monte, Rubidoux, Long Beach, and Upland sites from the SOCAB.
- The SCAQMD and the ARB sponsored a PM-10 sampling network, run by the California Institute of Technology, to measure PM-10 between December 1985 and August 1986. Carbon, ions, and elements have been quantified on the samples. Sampling sites were Burbank, Los Angeles, Lennox, Long Beach, Anaheim, Riverside, and San Nicolas Island. PM-2.5 was measured at the Los Angeles site. Chemical characterizations of particle emissions were also completed. The SCAQMD will apply source and receptor models to these data to estimate source contributions to PM-10.
- Dr. Glen Cass of the California Institute of Technology has recently completed a 15-day measurement program which acquired four-hour aerosol samples between 11 a.m. and 3 p.m. at Pasadena during the summer of 1984. These fine and coarse samples have been chemically characterized and are accompanied by detailed EAA, OPC, nephelometer, RH, T, HNO<sub>3</sub>, NH<sub>3</sub>, impactor, and SCAQMD gas data. The interpretation of these data is not planned for the near future, owing to lack of sponsorship.

photochemical reaction mechanisms for air quality models used in the SOCAB.

- CRC is sponsoring the development of a tunable diode laser to measure NO, NO<sub>2</sub>, HNO<sub>3</sub>, and HCHO at levels as low as 0.5 ppb. The builder of this instrument, Unisearch Associates, will field test it under polluted conditions typical of those in the SOCAB.
- CRC is sponsoring a project to develop a vehicle evaporative emissions model which estimates emissions from contemporary motor vehicles over a realistic range of operating and ambient temperature conditions. The model will produce more accurate estimates than current methods because it will include diurnal temperature profiles, individual fuel system component temperatures, control system-use pattern interactions, and weathering of tank fuel. This model is applicable to improvements of ROG emission rates in the SOCAB.
- CRC is sponsoring a study of the effects of oxygenates used in gasoline blending on evaporative emissions, with emphasis on ethanol and methanol-gasoline blends. A companion study is intended to determine the effects of fuel volatility, dispensed fuel temperature, and initial tank temperatures, dispensed fuel rate, and vehicle fuel system design on the magnitude of vehicle refueling emissions. Results are applicable to improvements of ROG emission rates in the SOCAB.
- The SCAQMD has recently completed a 1983 emissions inventory update for the SOCAB. The ARB is compiling a 1984 point source inventory and a 1985 planning inventory for the National Acid Precipitation Assessment Program which will include ammonia emissions. The next comprehensive inventory for the SOCAB is scheduled for 1987 with availability by mid-1990. This will be the basis for the SCAQS inventory.
- The Electric Power Research Institute (EPRI) is studying alternatives to the contrast method for determining light extinction in the atmosphere. The assumptions of visibility measurement methods have been examined and alternatives have been developed to eliminate several of the assumptions which are not met in normal situations. Modifications to the integrating nephelometer which minimize the alteration of suspended particles with respect to water, organic content, and size distribution have been explored. The results of these studies can be applied to visibility measurements in the SOCAB.
- EPRI is examining alternatives for the measurement of the liquid water content of suspended particles and constructing a calibration and audit standard for these methods. These methods are applicable to the quantification of liquid water in the SOCAB aerosol.
- EPRI has developed quality assurance and standard operating procedures as part of its regional air quality studies. These procedures have optimized maintenance and performance test schedules and contain appropriate data forms. They are available to be combined with other procedures for the development of a SCAQS procedures manual.

those mechanisms and measurements which have the greatest influence on model output. The adequacy of those choices is then tested through focused experiments. The results of those experiments then feed back into the model-building process. The models described here are in evolution even as this is written, and the perceived importance of the data they require will certainly change as new knowledge is gained.

To reiterate: no attempt is made here to prefer one model over another. By polling the modeling community, a common set of measurements has been defined which should be of utility to the future development of several modeling approaches and their ultimate use in making pollution control decisions.

### 2.5.1 Regression on Principal Components (RPCA)

The RPCA establishes an empirical relationship between atmospheric end-products, such as ozone and constituents of PM-10, by determining rotated eigenvectors of correlations among the causative variables. Linear regressions of the dependent variables on these factors are calculated. RPCA was first applied by Henry and Hidy (1979) to routine air quality data from the South Coast Air Basin, and they found photochemical, relative humidity, and dispersion/stagnation components to have varying influences on ambient sulfate levels. Since that application, several other studies have been published (e.g. Henry and Hidy, 1982; Liou et al., 1982; Wolff and Korsog, 1985; Malm, 1985; Chow and Spengler, 1985) which show the potential of this method. Chow (1985) provides the most recent summary of these applications and testing of this method.

The RPCA model produces mathematical factors which must be interpreted as physical factors based on the atmospheric variables included in the analysis. These variables need to be selected such that they will be surrogates for the important physical factors. Past applications of RPCA have been limited because these important variables have not always been available.

The important physical factors which are expected to affect oxidant and PM-10 concentrations in the South Coast Air Basin are: (1) primary and precursor emissions of particulate matter, NO<sub>2</sub>, reactive hydrocarbons and SO<sub>2</sub>, (2) photochemical transformation mechanisms, (3) heterogeneous transformation mechanisms, (4) transport and stagnation, (5) temporal variability of all factors, (6) emissions injection height, and (7) previous day carryover.

The observables which have been deemed important by their users for these RPCA models applied to oxidant and PM-10 concentrations are:

- sequential samples (of four to six hour maximum duration on consecutive days) of size segregated and chemically speciated particulate matter. Important species are geologically-related elements (Al, Si, Fe, Ti), other tracer components (e.g. Pb, Br, V, Ni, Cl, Na, elemental carbon, K), secondary products (e.g. total organic carbon, polar organics, sulfate, nitrate), and in situ liquid water content of the aerosol;
- hourly average oxidant, PAN, speciated reactive hydrocarbons, and NO<sub>x</sub>/NO<sub>2</sub> concentrations;

CMB might be an appropriate method for apportioning PM-10, and possibly the precursors of ozone, to their sources.

The CMB model consists of solutions to a set of equations which describe receptor concentrations of selected constituents as linear sums of the fraction of each constituent in source emissions times the total mass contribution of that source to the receptor. The receptor concentrations and source compositions are given to the model and the contribution from each source to each atmospheric constituent is calculated. Chow (1985) provides the most recent compilation of past applications while Watson (1979) presents the model assumptions and testing results. Other test results are reported by Currie et al. (1984) and Dzubay et al. (1984).

A recent evaluation of this model sponsored by the Electric Power Research Institute (Harold Javitz, SRI International, personal communication, September, 1985) concludes that although the CMB formulation is adequate for accurately determining many source contributions, even aggregate secondary contributions and the contributions to their precursors, this adequacy is extremely sensitive to the available observables and their random variability. The accuracy of current applications has been controlled more by the inadequacy of source profile measurements than by ambient measurements. There is no set of common source profile measurements in which all emitted species are characterized for all important sources. Chow (1985) and Edgerton (1985) have recently shown the value of including gaseous as well as particulate species measured in both the source and receptor samples. This increases the accuracy and precision of source apportionment and allows the gaseous species to be apportioned to their emitters. Very few current source profile measurements include the gaseous as well as particulate chemical constituents.

Although the CMB model can be applied to single samples of any duration, samples taken over shorter time periods provide more precise results in that they allow a better definition of contributing sources and a more accurate estimate of fractionation factors.

The important input data needs for the chemical mass balance model are:

- receptor particle measurements of key elements (Al, Si, Pb, Br, K, Cl, Na, V, Ni, Fe), ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ), organic and inorganic carbon, speciated organic materials, and individual particle characteristics in 0 to 2.5 and 0 or 2.5 to 10  $\mu\text{m}$  size ranges;
- receptor gas measurements of  $\text{NO}_x$ ,  $\text{SO}_2$ , CO, reactive and nonreactive hydrocarbons;
- source profiles for power plant, motor vehicle, refinery, resuspended dust, and marine aerosol which include gaseous and particulate observables specified above for all sources; and
- estimates of fractionation factors (after Stafford and Liljestrang, 1984) between source and receptor.

- improved speciation for both gaseous and particulate emissions. The same types of measurements should be made on all major source types and should include elements, ions, organic and inorganic carbon, sulfur dioxide, nitrogen oxides, ammonia, carbon monoxide, speciated gaseous and particulate organic species. Exhaust gases should be cooled, diluted and preferably aged prior to sample collection to approximate their compositions in the environment. Aggregate samples of area sources (e.g. motor vehicle emissions) are preferable to measurements of single sources. These measurements should be sufficient to determine ROG/NO<sub>x</sub> ratios for all sources. These speciations are needed both as input data for source models and for receptor models. Ammonia emission rates are also needed for aerosol models;
- accurate wind fields which account for the complex meteorological phenomena described earlier. These are critical to the establishment of effective cause-effect relationships between emissions and receptor concentrations. Additional locations and more frequent upper air measurements are needed to supplement and verify surface measurements;
- boundary and initial concentrations of oxidant and particulate species, and their precursors. These are needed to determine their evolution over a period of time. Of critical importance are the concentrations above the mixed layer during nighttime and morning periods. Concentrations over the ocean are required, and these may be at levels lower than those detected by conventional instruments which have been used previously. Hydrocarbon speciation and free radical concentrations are also needed at various sites to serve as initial concentrations and to verify model predictions throughout a simulated event; and
- intermediate reaction products. These are required to verify that chemical mechanisms are reproducing the multitude of chemical constituents which are actually observed during an episode.

## 2.6 SUMMARY

It is impossible to do justice to the wealth of information available regarding air quality in the South Coast Air Basin in a survey of this type. The emphasis here has been placed on learning from the past in order to gain in the future. The subsequent parts of this program plan have been influenced by these lessons, which can be summarized as follows.

- The value of simultaneous measurements of emissions, transport, transformation and receptor variables is far greater than the value of any of these measurements acquired at disparate places and times, and the cost effectiveness of simultaneous data collection exceeds that for separate studies.
- The physical and chemical understanding of the atmospheric processes affecting pollutant concentrations in the SOCAB is sufficient to define the observables which need to be measured, their averaging times, and the characteristics of episodes which are conducive to high pollutant concentrations.

### 3. MEASUREMENT APPROACH

This section describes the planned SCAQS field measurements. The measurement approach has been revised since the last version of the program plan (Blumenthal et al., 1986). Recommendations from participants, sponsors, and several working groups which were set up to design and review specific aspects of the study have been taken into account in the revised design. The planning activities, the role of the Field Manager, the measurement recommendations of the modeling community, and the rationale for selection of the sampling periods are summarized in Sections 3.1 through 3.3. The study includes a series of "core" measurements along with several complementary studies which address specific issues. The core measurements are described in Sections 3.4 through 3.7. Most of the special studies are described in Section 3.8; however, some of them are included in the list of A-site measurements in Section 3.4.

#### 3.1 PLANNING AND MANAGEMENT

##### 3.1.1 Planning Activities

The suggested program plan prepared in June, 1986 (Blumenthal et al., 1986) has been revised based upon three types of input. First, the suggested plan was widely distributed to the technical community and potential participants for their review and comment. Second, Emissions, Meteorology, and Model Working Groups were formed to review the plan and to recommend specific measurements and data collection activities which would meet the needs of the analysts and modelers who will use the data. Finally, the sponsors negotiated work statements with the participants who will perform the measurements listed in this section.

In light of the finite resources of the sponsors and limited technical feasibility of some of the measurements, compromises were made to arrive at the consensus program plan presented here. The final design process was an iterative effort with continual review by the Working Groups and the sponsors. Numerous meetings were held, and all points of controversy were pursued until a consensus was reached between the measurements participants, the working groups, and the sponsors. The detailed recommendations of the working groups are discussed in the remaining parts of Section 3 and are reflected in the study design.

##### 3.1.2 Field Management

The SCAQS field program will be coordinated by a Field Manager who will perform the following tasks:

- determine the power, space, and logistical needs of all field participants;
- arrange for access to the AQMD sites to be used during SCAQS;
- arrange for additional power and other necessary facilities;



- Free Radical Measurements: The Working Group studied in detail the question of which free radicals provide the most opportunity for evaluating our knowledge of the gas-phase chemistry and for discriminating among rival chemical reaction mechanisms. The conclusion arising from the studies is that measurements of peroxy radicals, namely,  $\text{HO}_2$  and  $\text{RO}_2$ , will provide the greatest amount of information concerning the detailed behavior of chemical mechanisms. Separate measurements of  $\text{HO}_2$  and  $\text{RO}_2$  would be best, but, if that is not possible, measurement of the sum of  $\text{HO}_2$  and  $\text{RO}_2$  is also of value. Although hydroxyl radical measurements have been proposed, these measurements are most useful in assessing the overall OH level in comparison with predicted levels. They will not allow differentiation of chemical reaction mechanisms since all mechanisms predict essentially the same OH levels.
- Hydrogen Peroxide Measurements: Hydrogen peroxide is a very sensitive indicator of  $\text{HO}_2$  levels and is an important species in its own right. Measurements of  $\text{H}_2\text{O}_2$  are viewed as essential.
- Formic Acid: Formic acid measurements would provide an important test of our understanding of the olefinic portion of reaction mechanisms. These measurements are encouraged.

The Working Group places a substantially lower priority on continuous nitric acid measurements than those listed above. However, as noted below, nitric acid measurements on the same time resolution as the aerosol nitrate and ammonia gas-phase measurements are essential.

In commenting additionally on the hydrocarbon measurements, the Working Group deems it very important to determine the total hydrocarbon cloud surrounding the Basin; namely, how far out and how high it extends. The question of marker compounds was discussed. It is important that the incoming air from the ocean be characterized with respect to its hydrocarbon level and composition.

Pilinis and Seinfeld (1986) used an air quality aerosol model to determine the sensitivity of the size and chemical composition of a simulated receptor aerosol to various input variables. Their studies result in the following recommended gas-phase measurements:

- $\text{SO}_2$  Aloft: Since more than 50% of the  $\text{SO}_2$  is emitted aloft from various point sources, upper-air  $\text{SO}_2$  concentration measurements are very important. Of special importance is the concentration of  $\text{SO}_2$  above the mixed layer overnight. This can be fumigated to the ground when the inversion layer grows the next day.
- $\text{NH}_3$  and Nitric Acid: Aerosol nitrate and nitric acid exist in equilibrium, and the aerosol nitrate concentration is dependent on the amount of ammonia present in the atmosphere. An increase of only 10% in the amount of ammonia can result in a substantial increase in  $\text{NH}_4\text{NO}_3$  in the aerosol phase.
- Temperature and Relative Humidity: Perturbations of 5 degrees C and 30% RH are common during the day in the Basin. Such perturbations can result

- Aerosol Physical Measurements: Detailed aerosol size distributions are needed for aerosol modeling. A combination of an electrical mobility analyzer, an optical particle counter, and a large-particle counter could supply hourly-averaged size-distribution data. It is most critical that these measurements be made at the source site (Long Beach) and the two receptor sites (Claremont and Rubidoux). These measurements could be supplemented with a classifier/CNC at the receptor sites.

### 3.2.3 Meteorological Measurements

Kessler et al. (1986) carried out a number of wind field generation calculations for the South Coast Air Basin. The first conclusion from those studies is that one cannot construct a good three-dimensional wind field from surface measurements alone; upper air data are crucial. The second major conclusion is that the current surface network proposed for SCAQS is adequate for generating a surface level wind field. With approximately six upper air measurements, the question is -- Where should these be made and how frequently? It was generally agreed that measurements in the interior of the SOCAB will be more useful than measurements in the outlying areas, for the purposes of data analysis.

### 3.2.4 Emissions Inventory

The ROG speciation of the inventory should be consistent with the two types of chemical mechanisms used today in photochemical modeling. The recommended compound classes for the two types of mechanisms are:

<u>Surrogate Species Mechanisms</u>	<u>Carbon Bond Mechanism</u>
C4-C5 Alkanes	Paraffinic Bonds
>C5 Alkanes	
Ethene	Ethene
Terminal Alkenes	Olefinic Bonds
Internal Alkenes	
Mono-alkylbenzenes	Mono-alkylbenzene Bonds
Di-alkylbenzenes	Di-alkylbenzene Bonds
Tri-alkylbenzenes	
Formaldehyde	Formaldehyde
Acetaldehyde	
Other Carbonyls	Other Carbonyls
Nonreactive	Nonreactive

The Systems Applications, Inc. Urban Airshed Model (UAM) has been applied extensively in the South Coast Air Basin utilizing a horizontal grid resolution of 5 km (Reynolds et al., 1973; Roth et al., 1984). Seigneur et al. (1981) demonstrated a significant deterioration in model performance in the SOCAB when the grid size was increased to 10 km; based on this result, 5 km should be considered to be the minimum resolution required for effective application of the UAM in this region.

The standard temporal resolution of UAM emissions inventories has been one hour. In general, data on point and mobile source emissions can be obtained with this temporal resolution. Frequently, only yearly rates are

Table 3-1. Percentage of Days for 1978-83 with Early Morning Clouds and Low Afternoon Visibility.

	Ceiling (0800 PST)		Visibility (1400 PST)	
	LAX ≤1800 ft.	ONT ≤1000 ft.	LAX ≤6 miles	ONT ≤6 miles
May 1 - 15	19%	16%	12%	49%
16 - 31	37	27	20	65
June 1 - 15	40	25	36	75
16 - 30	33	21	12	63
July 1 - 15	27	8	17	44
16 - 31	33	9	33	71
August 1 - 15	40	13	27	55
16 - 31	32	8	18	53
Sept 1 - 15	15	12	31	49
16 - 30	21	3	20	41
Oct 1 - 15	36	12	37	51
16 - 31	18	9	33	44

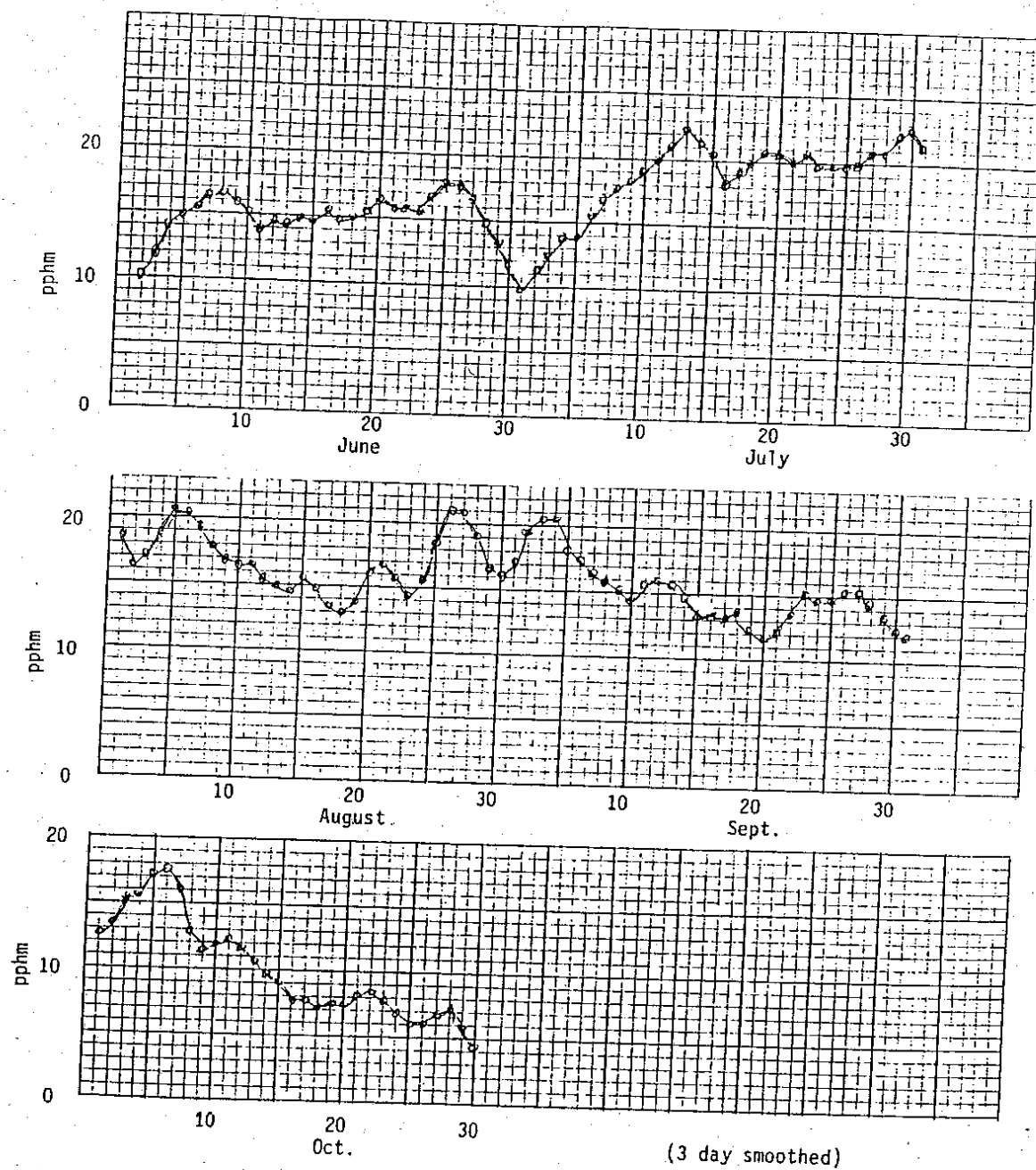


Figure 3-2. Maximum Ozone at Pomona. (Average of 1978-83.)

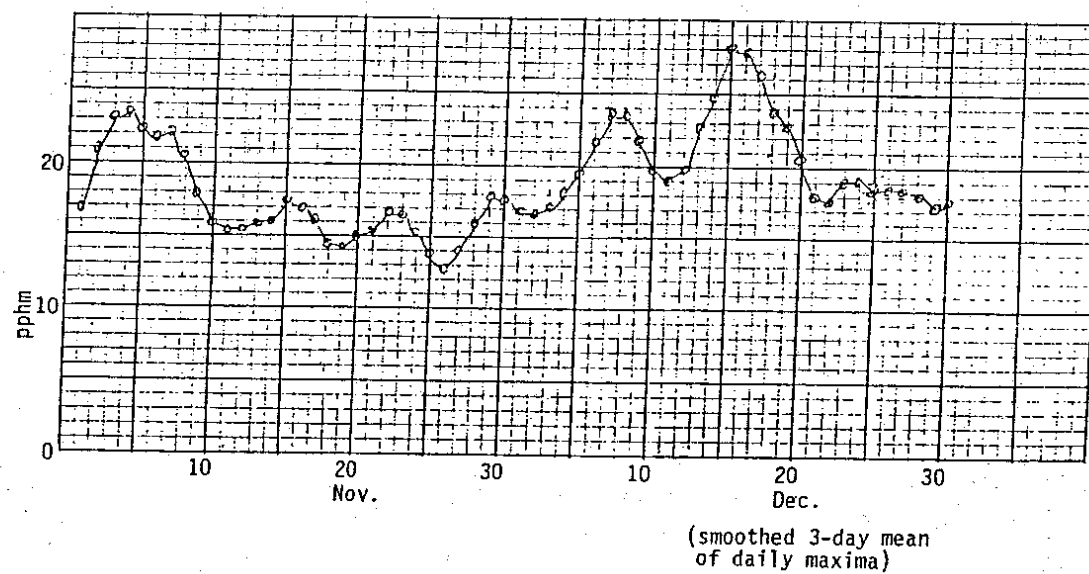
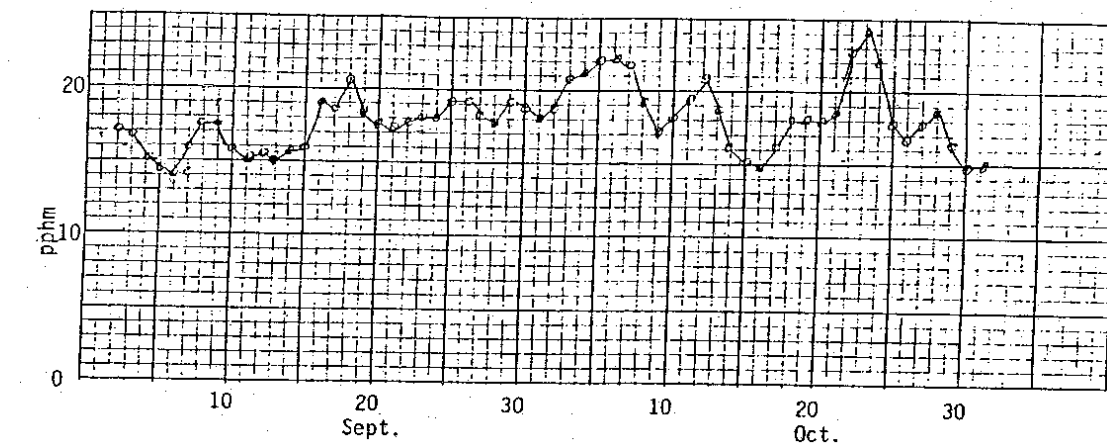


Figure 3-3. Maximum NO<sub>2</sub> - South Coast Air Basin. (Average of 1978-83.)

### A-Sites

A-sites will be the base of operations for selected intensive measurements, special experiments, and individual investigators. Long Beach and Claremont are the A-sites for the summer sampling period. These sites represent source and receptor regions respectively. Only the Long Beach source-oriented site is a A-site during the fall sampling period. A-site instruments are operated primarily on intensive study days, but some researchers will operate their equipment continuously.

### 3.4.2 SCAQS Air Quality Measurements and Measurement Methods

The observables to be measured at the A-, B-, and C-sites, the averaging times, and measurement frequencies are presented in this section.

#### C-Site Measurements

The C-site measurements consist of those air quality and meteorological variables which are normally measured by the Air Quality Management Districts. Table 3-2 summarizes these measurements, and the specific measurements at each station are identified in Table 2-3. The measurements methods and procedures at the C-sites are already in place and are quality assured by the Districts and the ARB on a regular basis. These data will be extracted from the Districts' data base for the SCAQS summer and fall sampling periods and integrated with the rest of the SCAQS measurements.

#### B-Site Measurements

All of the C-site measurements will also be made at B-sites throughout the summer and fall periods. The measurements to be made at the B-sites are identified in Tables 3-3a through 3-3f. The continuous measurements will be made on all days during the study period. The other measurements will be made only on the intensive sampling days. The measurement methods were selected after extensive evaluation of different alternatives with respect to reliability, sensitivity, cost, availability, and compatibility with existing measurements. Only brief reasons for selecting each method are given in the tables, since the entire selection rationale is too involved for presentation in this program plan. Table 3-3a also includes estimates of the ambient concentration, lower quantifiable limit, and precision for each measurement. In all cases the lower quantifiable limits are sufficient to measure the expected concentrations of the stated variables.

Detailed protocols for field and laboratory operations at B-sites are being prepared. The B-site field operations are summarized below. B-sites will be manned for 24 hours per day on intensive sampling days. Technicians will verify that all continuous monitoring instruments are operating properly and will change canisters and substrates on a defined schedule. A specially-designed gas and aerosol sampler (the SCAQS Sampler) has been constructed and tested for  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{SO}_2$  and the PM-2.5 and PM-10 chemically speciated sampling at B-sites. Media in the SCAQS Sampler will be changed at 0600, 1000, 1400 and 1800 hours local time (PDT in the summer, PST in the fall) and midnight standard time (0100 PDT in the summer, 2400 PST in the fall). The changes beginning at 0600 will help match these samples to the morning rush hour during both summer and fall. The change at midnight will allow these

Table 3-3a. Network Measurements at B-Sites  
(See Table 3-3f for abbreviations)

5/8/97	Observable	Dur- atm	No. per site-day	Mass. method	Ambient concentrations Typical	Units*	Lower quantifiable limit	Precision**	Reason for selection	References and notes
	<b>METEOROLOGY</b>									
	Wind speed	Cont.	24	Cup anemometer	3	m/sec	0.25	0.25	A	
	Wind direction	Cont.	24	Vane	IA	degrees	IA	3	A	
	Temperature	Cont.	24	Thermistor	IA	degrees C	0.5	0.5	A	
	Dew point	Cont.	24	Dew cell	IA	degrees C	0.5	0.5	A	
	UV radiation	Cont.	24	UV radiometer	30	watts/m2	0.5	0.25	A	
	<b>GASES (continuous)</b>									
	CO	Cont.	24	UV absorption	30	ppb	2	15%	A	
	NO	Cont.	24	Chemiluminescence	30	ppb	2	15%	A	
	NO <sub>x</sub>	Cont.	24	Chemiluminescence	50	ppb	2	15%	A	
	SO <sub>2</sub>	Cont.	24	Pulsed fluorescence	6	ppb	2	15%	A	
	CO	Cont.	24	NDIR	2	ppm	0.5	15%	A	
	<b>GASES (integrated sample)</b>									
	SO <sub>2</sub>	In the	5	Improp. filter	6	ppb	0.2	7%	C,E	1
	NH <sub>3</sub>	SCAGS	5	Densite tube	5	ppb	0.3	10%	D	2
	HNO <sub>3</sub>	Sampler	5	Densite tube	7	ppb	0.4	10%	D	3
	Carbonyls	1 hr.	3	DNPH absorber	3-7	ppb	0.5	10%	C	4
	C1-C10 HC	1 hr.	3	Canisters and GC/MS	0.1 to 50	ppb	0.1	10%	B	5
	PAH	1 hr.	24	In-situ GC/MS	5-10	ppb	0.5	15%	C	6
	H2O2	1 to 7 hr.	8	POHAA fluorescence	5 (est.)	ppb	0.5	3%	C	7
	<b>AEROSOL PHYSICAL PROPERTIES</b>									
	Size dist.††	Cont.	24	OPC (Climet 200, PMS ASASP-X)	IA	IA	Resolves diameter ratio of 1.8	10%	B	8
	Light scattering	Cont.	24	EAA	IA	IA	10	5mV for 10V/Ls.	E,F	9
	Data acquisition	Cont.	-	Micro-computer	350	Min-1	IA	10%	G	10
	<b>AEROSOL CHEMISTRY (in the SCAGS Sampler)</b>									
	PM-10/PM-2.5:	4 to 7 hr.	5	SA-25/Bondex 240	40	µg/m3	5.8	7%	B	11
	Mass	4 to 7 hr.	5	Gravimetric	5	µg/m3	0.05	7%	B	
	SO <sub>4</sub>	4 to 7 hr.	5	IC	8	µg/m3	0.03	7%	B	
	NO <sub>3</sub>	4 to 7 hr.	5	IC	3	µg/m3	0.1	7%	B	
	Cl-	4 to 7 hr.	5	IC	5	µg/m3	0.05	7%	B	
	NH <sub>4</sub>	4 to 7 hr.	5	AC	2.5	µg/m3	See Table 3-3b	5 to 20%	B,G,H	
	Elemental C	4 to 7 hr.	5	WDXRF	20	µg/m3	0.08	10 to 25%	D	
	Organic C	4 to 7 hr.	5	Thermal combustion	20	µg/m3	1.5	10 to 25%	D	
	Fine Sols.	4 to 7 hr.	5	Thermal combustion	20	µg/m3	1.5	10 to 25%	D	
	PM-10	24 hr.	1	LASER Int. plate on Nuclepore	50	µg/m3	5.8	7%	C,G	12
	Mass	24 hr.	1	SA-321A, quartz fit.	5	µg/m3	0.06	7%	A	
	SO <sub>4</sub>	24 hr.	1	Gravimetric	8	µg/m3	0.09	7%	A	
	NO <sub>3</sub>	24 hr.	1	IC	8	µg/m3	0.09	7%	A	
	<b>AEROSOL SIZE RESOLVED CHEMISTRY††</b>									
	SO <sub>4</sub>	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.4***	7%	D	
	NO <sub>3</sub>	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.8***	7%	D	
	Cl-	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.8***	7%	D	
	H+	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.8***	7%	D	
	NH <sub>4</sub>	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.8***	7%	D	
	NH <sub>4</sub> K+	4 to 12 hr.	4	Bernert LPI & IC	2	µg/m3	0.8***	7%	D	
	Elemental carbon	4 to 12 hr.	4	MOUDI & therm. comb.	0.5	µg/m3	0.8***	7%	D	
	Organic carbon	4 to 12 hr.	4	MOUDI & therm. comb.	0.5	µg/m3	0.8***	7%	D	
	Elements	4 to 12 hr.	4	MOUDI & PIXE	1.5	µg/m3	0.2***	10 to 25%	D	
	†† Units apply to both ambient concentrations and the lower quantifiable limit.									
	*** µg/m3 per stage									

†† Measurements made only at Claremont, Downtown L.A., Long Beach, and Rubidoux.  
††† Measurements made only at Claremont, Long Beach, and Rubidoux.

Table 3-3c. C<sub>1</sub> to C<sub>10</sub> Hydrocarbons  
Measured by GC/FID

Ethane	2,4-Dimethylpentane
Ethylene	Benzene
Acetylene	Cyclohexane
Propane	2,3-Dimethylpentane
Propene	3-Methylhexane
i-Butane	2,2,3-Trimethylpentane
i-Butane	n-Heptane
1-Butene	Methylcyclohexane
n-Butane	2,4-Dimethylhexane
trans-2-Butene	2,3,4-Trimethylpentane
2,2-Dimethylpropane	Toluene
cis-2-Butene	2,3-Dimethylhexane
3-Methyl-1-butene	2-Methylheptane
i-Pentane	3-Ethylhexane
1-Pentene	n-Octane
2-Methyl-1-butene	Ethylcyclohexane
n-Pentane	Ethylbenzene
Isoprene	p-Xylene
trans-2-Pentene	m-Xylene
cis-2-Pentene	Styrene
2-Methyl-2-butene	o-Xylene
2,2-Dimethylbutane	n-Nonane
Cyclopentene	$\alpha$ -Pinene
4-Methyl-1-pentene	i-Propylbenzene
Cyclopentane	n-Propylbenzene
2,3-Dimethylbutane	3-Ethyltoluene
2-Methylpentane	2-Ethyltoluene
3-Methylpentane	1,3,5-Trimethylbenzene
2-Methyl-1-pentene	1-Ethyltoluene
1-Hexene	$\beta$ -Pinene
n-Hexane	Myrcene
trans-2-Hexene	1,2,4-Trimethylbenzene &
1,3,5-Trimethylbenzene	sec-Butylbenzene
1,2,4-Trimethylbenzene	$\Delta^3$ -Carene
cis-2-Hexene	$\alpha$ -Terpinene
Methylcyclopentane	d-Limonene
	$\gamma$ -Terpinene
	Terpinolene



Table 3-3e. References and Notes.

1.  $\text{Na}_2\text{CO}_3$ /glycerine impregnated Whatman 541 cellulose fiber filter for sulfur dioxide. The lower quantifiable limit is small and the method has been characterized (Forrest et al., 1981) and used in the field.
2. Oxalic acid coated denuder tube with backup filter impregnated with oxalic acid (Ferm, 1979).
3.  $\text{MgO}$ -coated denuder difference method for nitric acid (Appel, Tokiwa, and Haik, 1981).
4. 2,4-dinitrophenylhydrazine (DNPH) absorbing cartridge for carbonyls (Levin et al., 1985; Fung and Grosjean, 1982).
5. Hydrocarbons are pumped into canisters for later laboratory analysis by GC/FID. There is less adsorption and desorption of hydrocarbons in electropolished stainless steel canisters than in bags (Grosjean and Fung, 1984).
6. Electron capture gas chromatography (EC-GC) for PAN (Stephens, 1969b). Units are calibrated and operated continuously in the field.
7. Para-hydroxy phenylacetic acid - horseradish peroxidase method for gas phase hydrogen peroxide (Lazrus et al., 1986; Kok et al., 1986; Heikes et al., 1985). Samples are collected in bubblers.
8. Climet optical particle counter, PMS ASASP-X, and electrical aerosol analyzer (EAA) determine aerosol size distribution data in the 1 to 10  $\mu\text{m}$ , .09 to 3  $\mu\text{m}$ , and 0.003 to 1  $\mu\text{m}$  size ranges, respectively.
9. Integrating nephelometer measures scattering of light by particles.
10. Microcomputer data acquisition system. Flexible and cost effective. Data can be recorded in a format which can be read by most laboratories, so adding data from other experiments is possible.
11. A specially designed aerosol sampling system has been constructed for SCAQS. The SA-254 size selective inlet is for <10  $\mu\text{m}$  particles (Olin and Bohn, 1983) and the Bendix 240 cyclone is for <2.5  $\mu\text{m}$  particles (Chan and Lippman, 1977) at 113 l/min flow rates.
12. Hi vol sampler with SA-321A 10  $\mu\text{m}$  inlet. This inlet may pass some large particles.
13. The MOUDI Impactor (Marple and Rubow, 1984) collects submicron particles in defined size ranges on aluminum foils for subsequent carbon analysis.
14. The DRUM Impactor acquires submicron-sized samples on mylar films which are submitted to PIXE analysis.

samples to match the every sixth-day 24 hour PM-10 samples, which are changed at midnight standard time year round. Carbonyl absorbers and hydrocarbon canisters will collect one hour samples starting at 0700, 1200, and 1600 local time; and hydrogen peroxide samples will correspond to the particle sampling schedule except that hourly samples will be taken from 1400 to 1800. High volume PM-10 samples will be of 24-hour duration and will be changed at midnight. MOUDI and Berner LPI samples will be changed at 0600, 1000, 1400, and 1800. The sample durations and changing times have been selected as a compromise between: 1) the amount of time needed to obtain a detectable deposit, 2) minimizing the number of samples to reduce costs, 3) manpower deployment among the different instruments, 4) correspondence of measurement periods, and 5) temporal resolution required for modeling and data interpretation. Though the schedule cited above is not perfect, it is a reasonable compromise between these five requirements.

The B-site stations can be operated by one trained technician. For intensive study days, two technicians working overtime will operate the stations continuously. Having the stations manned full time will enable immediate identification of problems and rapid correction. In addition, it removes the requirement for automatic sequencing of filter sample devices. The technicians will primarily perform the routine station operations and will not be responsible for repairs. A separate, highly knowledgeable technician will be on call for repairs, and spares for critical components will be available at a central location.

A data acquisition system is included in Table 3-3a under the Aerosol Physical Property heading. A personal computer-based system has been designed to control the aerosol equipment and to record all continuous data.

A simplified flow diagram of the SCAQS Sampler is shown in Figure 3-5. This sampler has been designed to meet the specific requirements of SCAQS for integrated fine- and coarse-particle chemistry measurements and coordinated gas-phase measurements of low-level ammonia, sulfur dioxide and nitric acid. The sampler has also been designed to make it easy for the technician to change media for sequential samples and to document all necessary parameters for each sample. Two sets of sampling cassettes will be available at each site so that the technicians can load cassettes between sampling periods and can quickly switch cassettes at sample change times. The cassettes and media holders used for sampling and transport are all color coded, and an extensive media documentation scheme has been developed to minimize problems from sample handling errors.

#### A-Site Measurements

The primary measurements planned for the A-sites during the summer are summarized in Tables 3-4a through 3-4c. The fall A-site measurements will be finalized later. Many of the measurements listed are quite experimental in nature and are really special studies in themselves. Some of the measurement methods indicated in the table are unique to one investigator or group. Table 3-4a is organized in the same fashion as Table 3-3a for the B-sites, except that ambient concentrations, lower quantifiable limits, and precision are not included, since most of the techniques are still experimental. The measurements listed in Table 3-4 were suggested by the sponsors and technical reviewers and were refined to reflect the consensus of SCAQS participants. The

Table 3-4a. Additional Measurements at A-Sites During the Summer  
(See Table 3-4b for abbreviations)

6/6/87	Observable	Duration	No. per site-day	Site(s)*	Potential meas. method	Reason for Selection
<b>GASES</b>						
	C1-C10 HC	1 hr.	3 more, 6 total	C, LB	Canister & GC/FID	A
	C2-C12 HC	3 hr.	1; 2	LB, LA, C	Canister & GC/FID	E
	Halocarbons	6 hr.	4	C	GC/EC	E
	Carbonyls	1 hr.	3 more, 6 total	C, LB	DNPH absorber	A
	Carbonyls	3 hr.	1; 2	LB, LA, C	DNPH absorber	A
	Methyl & ethyl alcohol	4 to 7 hr.	5	C, LB	Charcoal absorber/thermal/impinger/GC-EC	E
	Formic, acetic acid	4 hr.	6		Impreg. filter - IC	E
	HONO, HCHO, NO2	15 min.	80	C, LB	DOAS	B,C,F
	HNO3	4 to 7 hr.	5	C	DDMIC, TFR/IC, luminol detection	E
	H2O2, HNO3	Cont.	24	C	TDLAS	B,E
	PAN, NO2	4/hr.	24	C	GC/luminol	E
	HNO3, HNO2	4 to 7 hr.	5	C	Annular denuder, IC	E
<b>RADICALS</b>						
	NO3	15 min.	15	C, LB	DOAS	C
	RO	Cont.	24	C	Chem. amplifier	E,F
<b>ORGANIC AEROSOL</b>						
	EC, OC	2 hr.	12	C	Filter & thermal-optical	F
	Carbon 14 (PM-2.5)	24 hr.	1**	C, LB, R	Accelerator mass spec.	E
	Carbon 14 (PM-10)	24 hr.	1***	C, LB	Accelerator mass spec.	E
	Organics	4 to 7 hr.	5	C	LPI & FTIR	E
<b>INORGANIC AEROSOL</b>						
	Water			C, R	TDMA; heated nephelometer	E
	Acidity, SO4=	4 to 7 hr.	5	C	Titration & IC	E
	S speciation	Cont.	24	LB	Thermal/NH3 & FID	E
	SO4=, NO3-	4 to 7 hr.	5	C	Annular denuder & IC	E
	PM-10 ions	12	2	C	AC, AA	E
	Br, Pb	5 hr.	1	C	WDXRF	E
	Elements; EC, OC; SO4=, NO3-	4 to 7 hr.	5	C	Dicots & WDXRF; thermal combustion; IC	C,E
	SO4=, NO3-	15 min.	3	C	LPI & flash vapor/FPD, IC	E
	Elements	4 to 7 hr.	5	C, LB, R	IMPROVE & PIXE	E,F
	Dry deposition	12 hr. +	2	C	IC on surrogate surfaces & vegetation	E
	Coarse mass; SO4=, NO3-	24 hr.	1	C	Deposition plate/gravimetric; IC	E
	Coarse mass; SO4=, NO3-	4 to 7 hr.	5	C	Rotary impactor/gravimetric; IC	E
<b>AEROSOL PHYSICAL PROPERTIES</b>						
	Light absorption	Cont.	24	C	Spectrophone	E
	Light absorption	4 hr.	6	C	Filter reflectance	E,F
	Light absorption, abs. vs. RH	Cont.	24	C	Filter transmission (Aethalometer)	E,F
	Path transmittance & radiance	Cont.	13	C	Radiance difference	E
	Light extinction	Cont.	13	C	Telephotometer	E
	Size vs. RH, vs. reactive gas	15 min.	3	C	TDMA	E,F
	Light scattering vs. RH	15 min.	3	C, R	Heated nephelometer	E,F
	Detailed fine part. size distribution			C	Electrical classifier	E
<b>INDIVIDUAL PARTICLES</b>						
	Size & chem. comp.				Electron microscopy; microprobe; GC/MS	C,F
<b>OTHER</b>						
	Mutagens	24 hr.	1	C		E
	Toxic air contaminants	24 hr.	1	C, LB, LA, R	Canister & Tedlar bags- GC/FID	E
	Calif. Dry Deposition Sampler	12 hr.	2	C		E
	Operational Evaluation Network Sampler	12 hr.	2	C		E

\*For sites, C is Claremont, LB is Long Beach, LA is Los Angeles, R is Rubidoux.

\*\*Analyze only 24 of 36 samples.

\*\*\*Analyze only 7 of 24 samples.

Table 3-4c. Key to Reasons for Selection

---

A	Extension of measurements already made at B-sites.
B	This species also measured by instrument chosen to measure another species.
C	Method has adequate sensitivity, accuracy, freedom from interferences.
D	To increase the variety of elements determined.
E	Method provided by a sponsor.
F	Equipment availability.

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Table 3-5. Toxic Air Contaminants to be Measured in the Study Region.

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Benzene	Methyl bromide
Carbon tetrachloride	Methyl chloroform
Chloroform	Methylene chloride
Chlorobenzene	Perchloroethylene
Ethylene dibromide	Trichloroethylene
Ethylene dichloride	Xylene (o-, m-, and p-)

---

obtained for about 30-40 minutes in each orbit. Typically, the samples will be obtained in the inversion layer above the surface layer (about 1000' agl) in the morning and in the middle of the mixed layer in the afternoon (about 1500'-2000' agl).

For the fall sampling, one aircraft will collect integrated samples in addition to its continuous measurements. It will perform two flights per day in the morning (0500-0900 PST) and in the afternoon (1300-1700 PST). It will focus its measurements in the western portion of the Basin, performing spirals at about five locations as well as collecting integrated samples in orbits at two locations. The occurrence of fog will restrict some flights. Occasional night flights could be made when fog is not a problem.

In addition to the in-situ airborne measurements, airborne LIDAR measurements will document the three-dimensional pollutant distribution, especially along the slopes and offshore. In conjunction with the surface and upper air winds, the LIDAR will provide useful information on the fluxes into and out of the basin at the boundaries and on pollutant ventilation and carryover processes. LIDAR flights will be made in early morning and in mid-afternoon during intensive study days. The morning flight will document layers carried over from the previous day and will map the offshore boundary conditions. The afternoon flights will document the boundary conditions and ventilation processes.

### 3.6 EMISSIONS

Our discussions with the modeling community have indicated that the quality of the available emissions data is one of the limiting factors in improving model accuracy. For three-dimensional grid models, an accurate, gridded, time- and species-resolved inventory will be necessary for each day to be modeled. For receptor models, detailed characterizations of the emissions from different sources will be needed for source identification (especially organics and trace metals).

To address the overall emissions issue, an Emissions Working Group (EWG) was formed. The group consists of university, industry, and government members and is responsible for providing the SCAQS emissions inventory. The EWG will design and execute studies to examine the accuracy of existing inventories and will coordinate special studies to improve these inventories. The EWG members are listed in Appendix A.

Emphasis will be on those species most important for oxidant and aerosol formation including organic and inorganic gases and size-resolved particulate matter. The basis for the SCAQS inventory will be the scheduled 1987 inventory update for the South Coast Air Basin to be prepared by the SCAQMD and the ARB. This inventory will be refined as necessary to include the results of special inventory characterization studies and emissions information specific to the intensive days of the SCAQS field program. The characterization studies are aimed at quantifying and reducing the uncertainties in the inventory, and thus obtaining a more accurate characterization of emissions in the Basin. The EWG will work closely with both the SCAQMD and CARB during this process.

Table 3-7. Emissions Working Group Planning Study Topics

- 
1. Data Base Schedule
  2. Emission Inventory Preparation Process
  3. Results from Model Sensitivity Runs
  4. Motor Vehicle Emission Factors
  5. Stationary Source Emissions
  6. Aerosol Characterization Data
  7. Uninventoried Sources
  8. Small Hydrocarbon Sources
  9. Area Source Gridding
  10. Vehicle Use Data
  11. Evaporative Emissions
  12. Road and Soil Dust Emission Factors
  13. Temporal Resolution
  14. HC/NO<sub>x</sub> Ratio
  15. Two Versus One Data Bases
  16. Day-Specific Data Needs
  17. Inventory Uncertainties
-

### 3.7.2 Forecast and Decision Protocol

The forecasting team will issue a meteorology and air quality forecast each afternoon for the following two-day period. The forecast of PM-10 and ozone concentrations will be in terms of three categories, low, medium, and high, based on the historical distribution of ozone daily maxima and PM-10 24-hour average concentrations. The categories, with their associated cut points, are:

	High (75th percentile)	Medium (50th percentile)	Low
PM-10 (24 hr. avg.)	>105 $\mu\text{g}/\text{m}^3$	>88 $\mu\text{g}/\text{m}^3$	<88 $\mu\text{g}/\text{m}^3$
Ozone (max. hr.)	> 24 pphm	>19 pphm	<19 pphm

Days when either PM-10 or ozone are predicted to be in the high category, or when both are predicted to be in the medium category will be considered as acceptable for sampling.

The decision to start intensive sampling will be made by the Program Coordinator, based on the forecast and on the logistical readiness of the investigators and equipment. Nominally, the sampling periods will be for two days, but one- or three-day periods are possible. There will be at least a one day rest period between intensive sampling periods.

The decision to sample will be made after the afternoon forecast (about 1600 local time) for the sampling period which starts at 0000 PST the next night (about 32 hours later). If a decision to sample is made, the intensive sampling may be cancelled the next day after the forecast in the afternoon before the sampling is to start (~8 hours in advance).

For each intensive study day, meteorological summaries will be prepared which document cloud locations, bases, thicknesses, and durations; mixing height and inversion strength as available from temperature, wind, and acoustic sounder data; the synoptic conditions; and any unusual weather occurrences.

### 3.8 SPECIAL STUDIES

Some of the stated project objectives cannot be met with the monitoring data alone. Several special studies will be performed to address specific questions. Some of these are outlined below, but the details of their designs are not included in this plan. Most of these special studies are either self-contained data acquisition and interpretation projects or are enhancements to the existing SCAQS measurements.

#### 3.8.1 Perfluorocarbon and SF<sub>6</sub> Tracer Releases

Two types of tracer tests will be performed during the SCAQS summer sampling period. One series of tests will evaluate the relative impact of elevated and ground-level emission sources on ground-level concentrations of ozone, NO<sub>2</sub> and PM-10. Four unique perfluorocarbon tracers will be used for these tests. Simultaneous releases will be made from a 200 foot stack at



humidification chamber and size selective aerosol sampling to determine the response of carbonaceous species to changes in relative humidity. A reference which produces known quantities of liquid water will be available as a standardization and audit device for these measurements.

#### 3.8.4 Deposition Fluxes

Large particles deposit at the ground by gravitational sedimentation, while small particles and gases deposit by turbulent transport to and absorption at the ground. A rotary impactor will be operated at the Claremont site to determine the concentrations of large particles (greater than ten microns) which are potentially present for deposition. This will be accompanied by a greased deposition plate to measure the quantity of particles which actually reach the ground. Sedimentation velocities can be calculated from these two measurements for use as parameters in particulate modeling. Deposition fluxes of small particles and acidic gases will also be determined by measurements on aerodynamic surrogate surfaces and vegetation at the Claremont site. These deposition fluxes can be combined with the ambient concentrations to infer deposition velocities for fine particles and gases.

#### 3.8.5 Acidic Species Sampler Methods Evaluation

The ARB has conducted measurement method comparisons for nitrogenous and carbonaceous species. The acidic species comparison will be the third in this series of method evaluations. The B-site SCAQS observables include several which are also being incorporated into national and state dry deposition monitoring networks. Several non-SCAQS sampling and analysis systems will be compared during the SCAQS summer period with the collocated SCAQS measurements at Claremont. The transition flow reactor from EPRI's Operational Evaluation Network, EPA's version of the transition flow reactor, University of Denver's continuous nitric acid analyzer, ARB's dry deposition sampler, EPA's annular denuder, a turnable diode laser absorption spectrometer, a denuder difference method, and several other samplers will be operated simultaneously with the SCAQS sampler. Additional samples will be taken during non-intensive sampling periods to measure low as well as high pollution events. The data from this comparison will be used to evaluate the precision, accuracy, and validity of measurement methods used in SCAQS and in other studies.

#### 3.8.6 Visibility Measurement Comparison

SCAQS also will provide an opportunity for a visibility measurement methods comparison. Several of the measurements cited with respect to relative humidity noted in Section 3.8.3 will provide visibility outputs and will be useful in determining the effects of different instrumental changes in humidity on visibility measurements. The B-site babs and nephelometer measurements are also available for comparison. In addition, long-path measurements of transmittance and path radiance will be made using a radiance difference technique, and contrast measurements will be made with teleradiometers. The information from this comparison will be used to address Objective 6, dealing with the validity and uncertainty of measurement methods. It will also allow the testing of visibility modules in air quality models.

## 4. QUALITY ASSURANCE

### 4.1 QUALITY ASSURANCE OVERVIEW

Every measurement consists of four attributes: a value, a precision, an accuracy, and a validity (e.g. Hidy, 1985). The measurement methods described in the previous section are used to obtain the value. Quality assurance is the complementary part of the measurement process which provides the precision, accuracy, and validity estimates and guarantees that these attributes are within acceptable limits. The quality assurance component of SCAQS is essential to the attainment of Objective 1.

Quality assurance for the project will be a major responsibility of the Program Coordinator (PC). The PC must ensure that the final program design contains adequate quality control procedures and adequate external checks to assure that the data obtained will be adequate for their intended purposes. In addition, it is the responsibility of the PC to monitor the quality assurance activities during the project and to make certain that problems are rapidly identified and solved. A quality assurance program will be implemented for all repetitive measurements for which a standard operating procedure (SOP) can be developed.

The quality assurance program for SCAQS will include two types of activities: quality control (QC), and quality audits (QA). The QC activities will consist of written standard operating procedures to be followed during sample collection, sample analysis, data processing, and auditing. These procedures define schedules for periodic calibrations and performance tests. They specify pre-defined tolerances which are not to be exceeded by performance tests and the actions to be taken when they are exceeded. The QC activities are on-going activities of measurement and data processing personnel. The QC procedures will be developed, documented, and implemented by each measurement group, and reviewed for completeness by the quality auditor.

Quality auditing is an external function performed by personnel who are not involved in normal operations. The purpose of quality audits is to determine whether the QC procedures are adequate and are being followed and whether the tolerances for accuracy and precision are being achieved in practice. The quality auditing function consists of two components: systems audits and performance audits.

Systems audits will be performed for all measurements. They start with a review of the operational and QC procedures to assess whether they are adequate to assure valid data which meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine whether the procedures are being followed and the operational people are properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data rather than a judgmental activity.

Performance audits (PA) establish whether the predetermined specifications are being achieved in practice. For measurements, the PA

- coordinate performance audits on routine measurements during the field programs;
- for any problems identified in audits, inform the PC and review the issue with the investigator until auditor and investigator agree on the existence and extent of the problem. Try to determine a course of action for remedying the problem;
- prepare short letter audit reports for the PC and investigators within 2 or 3 days of each audit; and
- prepare detailed draft reports for the PC and investigator for each audit. Revise drafts after feedback from the PC and investigator. Submit final audit reports to the PC for inclusion in the data base.

#### 4.3 DEFINITIONS

In developing a quality assurance plan, it is important that the project participants agree on the definitions of the terms used. These definitions are continually evolving (e.g. Mueller, 1980; Mueller and Hidy et al., 1983; Watson et al., 1983; Hidy, 1985), but the set to be used during SCAQS is presented below. These definitions will place all SCAQS measurement processes on a common basis.

- **Measurement:** An observation at a specific time and place which possesses four attributes: (1) value--the center of the measurement interval; (2) precision--the width of the measurement interval; (3) accuracy--the difference between measured and reference values; and (4) validity--the compliance with assumptions made in the measurement method.
- **Measurement Method:** The combination of equipment, reagents, and procedures which provide the value of a measurement.
- **Quality Assurance:** A combination of procedures, reference materials, and controlled tests which assure the precision, accuracy, and validity of the measurement and minimize the exceedance of pre-set tolerances for these attributes.
- **Quality Control:** Internal procedures, documentation, and performance tests which: (1) identify deviations from measurement assumptions and (2) identify measurement values which exceed pre-set tolerances when compared to internal reference materials. Quality control identifies and corrects measurement method deficiencies and provides the information needed to assign the precision and validity attributes to the measurement.
- **Quality Audit:** External procedures, documentation and performance tests which: (1) determine the adequacy of internal procedures, documentation and performance testing, (2) ascertain the degree to which internal quality control is following the prescribed procedures, and (3) challenge the measurement methods and internal reference materials with known values derived from an external reference material. Quality auditing identifies quality

or standards, little or no inter-method comparison results, and unknown precision, accuracy and validity.

- Measurement Process: Established or semi-established measurement methods combined with quality control and quality auditing to provide values with known precision, accuracy, and validity.

#### 4.4 STANDARD OPERATING PROCEDURES

Standard Operating Procedures (SOPs) codify the actions which are taken to implement a measurement process over a specified time period. These are both descriptive and prescriptive. The various SOP revisions are maintained so that subsequent users of the measurements may consult them to interpret measurements in light of new knowledge about the measurement methods being applied. Examples of this descriptive use were given in Section 2.2. The prescriptive role of SOPs is to incorporate state-of-the-art knowledge into current measurement practice. SOPs must undergo scheduled revisions in order to fulfill this prescriptive mandate.

Standard operating procedures will be created for routine field sampling, laboratory analysis, data processing, and quality audit activities planned for SCAQS. These procedures should include the following elements:

- A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions which must be met for it to be valid.
- A list of materials, equipment, reagents and suppliers. Specifications should be given for each expendable item, and its storage location should be listed.
- Designation of an individual to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- Startup, routine, and shutdown operating procedures and an abbreviated checklist.
- Copies of all data forms with examples of filled out forms.
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- Internal calibration and performance testing procedures and schedules.
- External performance auditing schedules.

should contain flags to identify the level of validation which they have received at any point in their existence.

## 5. DATA MANAGEMENT

### 5.1 ROLE OF DATA MANAGER

The Data Manager (DM) will be responsible for assembling, archiving, reviewing, and distributing the data obtained during the study. Specifically, the DM will perform the following tasks:

- With the concurrence of project participants, develop a data exchange protocol. All participants must agree to abide by the protocol in order to use study facilities and to obtain data from the data archives before publication of the final report.
- With the help of the participants, identify all data to be considered part of the study. (Some participants or other groups may obtain data for their own use which are unrelated to the study.)
- Develop standardized data formats with the assistance and approval of the participants. All participants will submit their data to the DM in the agreed upon format and media after each study period.
- Review all data submitted to determine that formats are proper and documentation is adequate.
- Identify sources, formats, and quality of data available from existing data resources (National Weather Service, Federal Aviation Administration, AQMD, etc.) and prepare a list of data to be obtained for the study.
- For each sampling day, obtain routinely available data, convert to project format, and archive.
- For each intensive study day, obtain all project data.
- Archive all data in an easily reproducible and retrievable form. The data should be archived using a disk-based data base management system so that data required for specific analyses can be easily accessed.
- Perform simple consistency and validity checks (Level II) on the data submitted, and flag those data points which are suspect. When possible, review suspect data with the responsible group and resolve the status of the data.
- Correct or flag data points in the master data base when errors are identified by subsequent users of the data.
- Prepare a report which inventories the data base for each study period and which documents the data formats and data access procedures. Summaries of data capture rates and data validity should be included for each intensive study period. Provide report to all participating and sponsoring organizations.

### 5.3 ACQUISITION OF SUPPLEMENTAL DATA

The DM with the assistance of ARB staff will be responsible for identifying and acquiring existing supplemental data. These data include NWS, FAA, and other available meteorological data and air quality data from SCAQMD, ARB, Ventura County Air Pollution Control District and other available sources. Such data obtained by the DM will be reformatted to be consistent with the core database formats for similar types of data. Potential sources of supplemental data are identified in Section 2.

### 5.4 DATA EXCHANGE PROTOCOL

A data exchange protocol has been prepared with input from the sponsors. The purpose of the protocol is to ensure timely and complete availability of the data collected as part of SCAQS and proper attribution for data used in analyses and publications. It will be a condition of participation in the program that sponsors and participants agree to abide by the protocol.

The approved protocol is shown in Figure 5-1.

## 6. DATA ANALYSIS AND INTERPRETATION

### 6.1 ROLE OF DATA ANALYSIS COORDINATOR

In a study of this type with many investigators and many types of data analysis and interpretation, it is necessary to have one person who can keep track of the project objectives and coordinate the diverse analysis efforts so that the objectives are met. The Data Analysis Coordinator will have the following tasks.

- Identify data analysis methods to meet each of the final project objectives.
- Identify the participant who will perform each analysis task.
- Identify the information and data needs for each analysis task.
- Work with the various investigators to develop a critical path diagram and identify when the investigator will need which information or data.
- Identify milestones for review.
- Act as a facilitator to assure that the required data are made available to the investigators on schedule and that investigators are aware of complementary efforts by other investigators.
- Identify duplications of effort and work out agreements between investigators to minimize unproductive efforts and maximize the technical output from the resources available.
- Identify topics for presentation at a technical session and coordinate with the investigators to assure that papers are presented on all appropriate topics.
- Synthesize and integrate individual data interpretation efforts into a coherent whole.
- Assemble and edit technical papers in a published document.

### 6.2 DATA INTERPRETATION METHODS

Measurements, by themselves, say nothing about the causes of air pollution and the likely effects of emissions reductions. It is only when these measurements are interpreted that relationships can be observed and conclusions can be drawn. The data interpretation methods which address the objectives stated in Section 1 need to be defined, at least in a general manner, before the first measurement is taken in order to assure: (1) that all information needed by the method will be available at the interpretative stage; and (2) that scarce resources will not be expended on taking measurements which do not fit within the data interpretation framework.

Section 1 stated the issues which might be resolved by SCAQS. Section 2 specified the additional data needs which model developers and users feel are



- Source oriented models contain mathematical descriptions of the interactions among variables. These models include transport and chemical mechanisms. Lloyd et al. (1979), Reynolds et al. (1976), Cass (1979), McRae et al. (1982a), and Seigneur et al. (1983b) have produced and tested such models appropriate for the SOGAB. Each of these source models requires three-dimensional wind fields (speed, direction, and dispersion characteristics at all points in the modeled area) over a period of one day or more. These wind fields can be interpolated from measurements (e.g. Goodin et al., 1980) or calculated from fundamental physical equations applied to a set of initial conditions (e.g. Pielke, 1984). Although the transport and chemical components are usually combined in the computer implementation of each model, it is possible to introduce alternative wind fields to simulate the transport mechanisms and alternative photochemical and aerosol mechanisms to simulate chemical interactions.
- Receptor models use chemical and physical measurements of sources and receptors. They require input data for the chemical compositions of the emitting sources and ambient concentrations of those same chemical species. Linear regression of species on principal components has been shown to relate sulfate concentrations to physical causes (Henry and Hidy, 1979). Chemical mass balance calculations (Gartrell and Friedlander, 1975; Miller et al., 1972; Cass and McRae, 1983; Feigley and Jeffries, 1979) can be applied in the SOGAB to determine the contributions of source emissions to receptors. Linear regressions of  $b_{scat}$  on selected chemical species or on source contributions can be applied to determine visibility extinction budgets (White and Roberts, 1977; Pratsinis et al., 1984).

Each of these data interpretation approaches has been designed around available data, with certain assumptions being made to compensate for the missing data. Most computer implementations of these models are quite flexible owing to their intended applications in many areas with varying data availability. There is no absolute list of data needs for any of these data interpretation methods. Presumably, the more data they have the better. In several cases (e.g. Seigneur et al., 1981a, 1981b), the effects of more or less data on the results of the data interpretation method have been evaluated. There is as yet, however, no objective means of defining the optimum set of data required by a data interpretation method, nor is it possible to generally determine when additional measurements would be redundant (unless those measurements are already available).

### 6.3 DATA USES

Data can be used for four purposes in the data interpretation process:

- Input data. Every interpretation method requires some data on which to operate for the period of time being examined. Descriptive methods require values of the variables of interest in space and time. Source models require boundary and initial conditions of precursor, intermediate, and end-product species as well as three-dimensional wind fields and atmospheric stability estimates. Receptor models require ambient concentrations and source composition. When these variables are measured for the time being simulated, they are considered input data.

spatial scales of the data interpretation methods can be used to estimate the uncertainty of input data and parameters. These uncertainties can also be estimated from periodic performance tests of each measurement method (Watson et al. 1983). It is presumed that future model development will include methods to take advantage of this information and supply intervals associated with measurement uncertainty on model results.

#### 6.4 SCAQS DATA INTERPRETATION PROJECTS

The measurements proposed in Section 3 can be used in an infinite number of combinations as input, to estimate parameters, to test the principles and assumptions of the data interpretation methods, and to estimate the uncertainty of the quantitative results of the interpretive efforts.

Data interpretation projects are described in this section which address the objectives and issues in Section 1. The projects which follow cannot identify every way in which the SCAQS data can be interpreted. The project descriptions are presented as examples to demonstrate that each piece of data collected does have a use for input, parameterization, testing, or uncertainty estimation. Although these projects are organized by the specific objectives and issues which they are intended to address, most of them are applicable to more than one objective.

Although Sections 2, 3, and 6 appear as separate entities in the program plan, they were actually formulated in an iterative fashion. Previous research in the SOGAB was studied to determine which data interpretation methods had been used in the past and the measurements they required. These were used to define an initial set of variables to be measured in SCAQS. These measurements were then incorporated into an interpretive framework which ultimately resulted in the projects described below. The measurement set was then modified to accommodate the anticipated data interpretation needs. This iterative process is not perfect, and it may still be found that the SCAQS measurements are not totally adequate for all purposes which might be identified a posteriori. It is expected that the number of these cases will be minimized, but not eliminated, by this iterative process.

##### 6.4.1 Objective 1: Description of SOGAB Air Quality

The data base will contain individual numbers which have been validated, corrected, and flagged. In order to be of use to researchers, this data base needs to be described statistically, graphically and phenomenologically. While most researchers will do this to a certain extent by themselves, a number of summaries have been produced in past studies which have been useful in focusing the more detailed analysis of specific situations. The data description projects are intended to provide this common denominator for subsequent projects. It is recognized that no "descriptive" study can be separated from the posing and testing of hypotheses based on previous work, and it is expected that the researchers performing projects intended to address the first objective will implicitly address other objectives as well. No attempt is made to exclude this possibility in the descriptions of the SOGAB air quality data. This speculation on cause and effect relationships is considered a "bonus" of an otherwise mundane presentation of results.

and temporal distributions of variables have been generated on a microcomputer and recorded on video tape or a video disk. Hussey et al. (1983) applied this method to air pollution data from the SOGAB with striking results. Henry (personal communication with Ron Henry, USC, 1985) is investigating its use in visibility studies. The adaptation of such a graphics display to microcomputers and interfaces to the commercial software packages described earlier would facilitate data interpretation in the SCAQS and leave a lasting legacy for subsequent air quality measurement programs.

Project 1.2: Meteorological and Upper Air Descriptions. Describe in detail each of the episodes obtained from the SCAQS in the style of Smith et al. (1972, 1984) and Blumenthal et al. (1978). These descriptions of the meteorological evolution will provide a qualitative understanding of the transport situation, convergence zones, the potential for mixing from aloft, and carryover from previous days. This qualitative description can be used to test the assumptions of the quantitative mathematical models describing transport in the basin. Surface trajectories can be inferred from the surface wind plots. Draw cross-sections of observable values obtained from aircraft vertical soundings and estimate mixing heights. Plot isopleths of mixing height for each aircraft sampling period. Examine the synoptic weather maps and correlate with the surface and upper air observations. Examine the differences between daytime and nighttime spatial distributions and determine outflow and ventilation scenarios. Compare the SCAQS descriptions with those of earlier studies such as Blumenthal et al. (1978), Smith et al. (1972), Angell et al. (1976), and Edinger (1959, 1973).

Project 1.3: Aerosol Data Descriptions. This project consists of the examination of the chemical, spatial, temporal, and size distributions of ambient aerosols, the comparisons of ostensibly equivalent methods of aerosol measurement, and the comparison of the SCAQS aerosol distributions with those derived in previous studies of Whitby et al. (1972), Hidy and Friedlander (1972), Heisler et al. (1973, 1980), Hering and Friedlander (1982), and Stelson and Seinfeld (1981). Calculate the material balance of the fine and coarse mass for each sample by converting elemental, ionic, and carbon measurements to probable compounds, summing, and ratioing to the gravimetrically measured mass concentration. Display these ratios as a time series and identify those which differ substantially from unity. Sum the four-hour total masses and ratio to the TSP mass concentrations for simultaneous samples. Produce pie charts which show the relative contributions of different chemical species to each fine and total mass concentration. Locate these pie charts on maps of the Basin with radii proportional to the total mass concentration at a site, similar to the display in Shah (1981). Identify the predominant size range of measured chemical species and compare with earlier findings. Plot four hour average number, surface area, and volume distributions as a function of particle size as derived from electrical mobility and optical particle counter data. Identify commonly recurring size distributions. Classify each sample according to one of the size distribution patterns. Plot the mass median diameters and standard deviations for each mode of the volume distributions on maps for each sampling period. Describe the evolution of the size distributions by location and time of day and compare to hypotheses advanced in previous studies such as Whitby et al. (1972), Hidy and Friedlander (1972), Heisler et al. (1973), and Heisler and Friedlander (1977). Examine similar size distributions and temporal/spatial plots using the

**Project 2.2: Source Profile Fractionation.** Using simple equilibrium, reaction, decay, and deposition considerations (e.g. Stafford and Liljestrang, 1984), calculate the expected changes in source profiles as a function of meteorological variables and the presence of other species. Coordinate with source-modeling projects to obtain a better description of source profile evolution from the more comprehensive chemical transformation mechanisms included in these models, and compare the simple transformation estimates with these more complex ones. Calculate transport times below which no significant fractionation will have taken place and beyond which equilibrium will have been reached. Select those species for which fractionation estimates are reasonably robust. Select cases, using the results of Projects 1.1, 1.2, and 1.3, in which the constituents measured at one of the source-area sites follow a trajectory passing over several monitoring stations, and calculate the expected changes in the combination of source profile for the selected chemical species. Apply the CMB at each site along the trajectory. Linear combinations of fresh and aged source profiles, weighted by emission rates from the emissions inventory, should be constructed and applied to determine their value in the transport region for which equilibrium has not been reached. Determine the variability of the calculated source contributions to PM-10, NO<sub>2</sub>, CO, hydrocarbons, and toxic substance concentrations as a function of the variables included in the CMB. Randomize the input data in proportion to their uncertainties and estimate the uncertainty which can be tolerated. Determine the collinearity of source profiles for various source contribution levels. Compare the effectiveness of source attribution by this method for highly reactive and non-reactive sampling periods.

**Project 2.3: Attribution of PM-10 to Primary/Secondary and Natural/Anthropogenic Sources.** Using the results of projects 2.1 and 2.2, construct source profiles for primary and secondary categories. Primary source profiles may consist of a number of individual source type profiles. Secondary source profiles may consist of those produced by several different conversion pathways. Similarly, construct source profiles for natural and anthropogenic source types. Apply the chemical mass balance receptor models to aerosol and gas data collected at urban and non-urban sampling sites for both the fall and summer periods and for the year-long 24-hour sampling periods. Calculate the contributions of each source type to the twenty-four hour and annual average concentrations of PM-10. Examine CMB diagnostics to determine the validity of each application. To determine the uncertainty of source attribution, compare the results derived from: (1) different combinations of sources and chemical species applied to the same receptor data, (2) randomized values for the receptor and source measurements, and (3) source apportionments derived from source models applied to the same samples.

#### 6.4.3 Objective 3: Dependence of Particle and O<sub>3</sub> Formation on Meteorological and Precursor Variables

**Project 3.1: Principal Components Analysis.** Develop a list of phenomena which can be represented by each SCAQS variable. These phenomena may be different for the same observable measured at a different place or time in the SCAQS network (e.g. NO<sub>2</sub> measured at night or during the day, at ground level or above the inversion, etc.). Submit these variables, excluding particulate matter and O<sub>3</sub> concentrations, to principal components analysis (e.g. Henry and Hidy, 1979). Apply the PCA to various subsets of variables to (1) obtain a stable solution and (2) determine the variability within a stable solution

Examine aircraft traverses and compare ozone,  $\text{NO}_x$ , and hydrocarbon concentrations to simple equilibrium calculations similar to those of Calvert (1976a, 1976b). Examine nighttime concentrations of  $\text{O}_3$  and precursors above the inversion and off the coastline to determine the degree of carryover from the previous day. Compare  $\text{ROG}/\text{NO}_x$  ratios with those calculated from localized emissions grid squares near the western and southern sites; identify potential causes of the discrepancy. If documentable day-to-day changes in emissions patterns (temporal and spatial) occur, compare the oxidant and hydrocarbon concentrations among otherwise similar meteorological conditions (e.g. Davidson and Cassmassi, 1985). Compare oxidant values in cases with high ambient aromatic hydrocarbon concentrations to values obtained when aromatic hydrocarbon concentrations are low.

Project 3.4: Case Studies on Aerosol Sulfate, Nitrate, and Carbon Formation. Calculate equilibrium concentrations for sulfur, nitrogenous, and organic species in the gas and particle phases for each sampling site and time and compare with the aerosol measurements. Examine fine and coarse particle chemical compositions, and infer the compounds which are present. Verify these inferences via single particle analysis of selected filter samples and determine the extent to which the aerosol is internally or externally mixed. Stratify ground-based and airborne measurements by day and night and compare chemically speciated size distributions and their changes with respect to time, thereby testing the hypotheses of Richards (1983). Examine speciated particulate and gaseous concentrations of organic compounds to estimate the fractions of organic carbon which are of primary and secondary origins. Coordinate with Projects 2.1 and 2.2 to perform this primary/secondary attribution of organic carbon.

#### 6.4.4 Objective 4: Dependence of Pollutant Spatial Distributions on Emission Height and Meteorology

Project 4.1: Case Studies of Natural and Injected Tracer Data. Examine the results of Projects 2.1 and 2.2 to differentiate between the primary emissions from elevated and ground level source at near-source and far-source receptors. Compare these estimates with the concentrations of perfluorocarbons and  $\text{SF}_6$  injected at high and low elevations. Examine the vertical concentrations above ground stations to determine gradients which might be caused by elevated source emissions, and determine which sources might be the cause from the elevated emissions maps produced in Project 1.1. Examine aircraft measurements above sampling sites along well-defined trajectories between source and receptors to determine the travel time required for vertical mixing of elevated source emissions. Stratify this travel time by atmospheric stability categories, and identify significant differences. Estimate the quantity of ozone,  $\text{NO}_x$ , particulate matter, and hydrocarbons which are contributed to surface concentrations by mixing as the inversion rises; and estimate the vertical distance for which vertical homogeneity is achieved as a function of time of day. Compare the results of this analysis with the assumptions of source models, and determine those cases for which the model assumptions would be valid. Examine speciated hydrocarbon and CO concentrations during high and low temperature periods to infer higher or lower evaporative fuel emissions as a function of temperature; normalizing hydrocarbon species with respect to CO may minimize the effects of different weather conditions on absolute hydrocarbon levels.

the accuracy, precision, and validity of the SCAQS sampling methods for acidic species, organic and inorganic carbon species, particle liquid water measurements, labile species measurements, and particle size measurements. Quantify differences between methods by non-parametric statistical tests, comparisons of uncertainty intervals, and linear regression analysis. Attribute differences between measurement methods which exceed precision intervals to standardization, interferences, sample validity, or other causes.

Project 6.2: Estimate Uncertainty of SCAQS Measurements. Combine the data from simultaneous measurements of the same observable by different methods and the results of measurement evaluations to quantify the variability about the measurement which would be found in a representative volume around the sampling point. List all of the assumptions which must be met by each measurement method in order to yield a valid value, and identify those periods of SCAQS sampling in which those assumptions were not complied with. Quantify the effects of deviations from these assumptions wherever possible.

## 6.5 COMPLEMENTARY MODELING PROJECTS

Although air quality modeling is not an integral part of SCAQS. The study has been designed to meet modeling needs. Several sponsors already have planned modeling uses for the SCAQS data and have made their data needs known during the planning process. These needs have been accounted for in this plan. In addition, the Model Working Group (MWG) was established to provide continuing technical input to the SCAQS design process. The MWG has served as an interface to the modeling community to assure that SCAQS data will be appropriate for modeling projects and to coordinate the modeling efforts of various participants.

The MWG has reviewed the current status of photochemical models (Seinfeld et al., 1987) and has made several recommendations for model improvements which should be made in anticipation of and using the SCAQS data. These recommendations are summarized in Section 6.5.1 below. Some of the modeling projects currently planned by the sponsors are summarized in Section 6.5.2.

### 6.5.1 Modeling Recommendations of the Model Working Group

Modeling Project 1: Improvements in Wind Field Descriptions. Currently, the major data inputs to primitive equation hydrodynamic models are synoptic geostrophic wind profiles (which can vary with time) and domain-scale initial profiles of temperature and moisture. These data are obtained from the NWS rawinsonde network which has a 12-hour temporal resolution and a spatial resolution on the order of 500 km. Given these initial domain-scale measurements, the primitive equation models calculate mesoscale fields of wind, temperature and moisture without mesoscale observational input. The high-quality SCAQS mesoscale observations can be used in conjunction with prognostic primitive-equation models. The resultant meteorological fields derived from the models should be superior to those obtained via either objective analysis of observations or from the model without such input data.

The SCAQS meteorological data can be used in two ways. In the first approach, the mesoscale model is run with the usual NWS derived initial conditions. Model results and observational data are then input together to an objective analysis algorithm which produces a set of "ultimate" gridded

similar, as expected since they are both based upon the laboratory kinetic, mechanistic and product data available. However, certain portions of the mechanisms, for example, those dealing with the aromatics chemistry, are different due to differing methods of parametrizing these presently unknown reaction mechanisms. At the present time, the major areas of uncertainty in the chemical mechanisms are those concerning the reactions of the aromatic hydrocarbons, the reactions of the longer chain alkanes, and of the ozone-alkene reactions.

The complete chemical mechanisms must then be tested against environmental chamber data. Uncertainties in the chamber light intensities and spectral distributions, and in the chamber effects (for example, the chamber dependent radical source and  $\text{NO}_x$  and organic off-gassing rates), together with the uncertainties inherent in the environmental chamber data themselves, lead to additional overall uncertainties in the predictive abilities of the chemical mechanisms. At the present time, the two latest mechanisms (the ERT/SAPRC and the Carbon Bond IV) agree with the environmental chamber maximum ozone yields to within approximately 30 percent. With reanalysis to take into account a reevaluation of the light intensities and spectral distributions of the University of North Carolina chamber, this 30 percent scatter may be reduced somewhat.

When used in urban airshed computer models for hydrocarbon control strategy applications, however, these two chemical mechanisms lead to different conclusions with regard to emissions reductions. SCAQS data should be used to compare against the intermediate reaction products of these mechanisms in order to resolve these differences.

Also, the performance of the several models which will be applied to and tested against SCAQS data should be compared. A protocol for such a comparison should be formulated, and the model applications should be designed such that a common set of performance measures is produced by each model.

Model Project 5: Transport/Deposition in Air Quality Models. A gap exists between the micrometeorology in air quality models and that in state-of-the-art planetary boundary layer models, and the treatment of micrometeorological phenomena in the air quality models applicable to the SOCAB should be improved. Dry deposition modules in these air quality models should be brought up to the most current level possible.

There is considerable room for improvement in the mixing layer determination and boundary-layer profiling in air quality assessment models. There also appears to be a need to adapt the models to more fully utilize the micrometeorological outputs from prognostic meteorological models. Improved micrometeorological data would improve the dry deposition velocities as well as the  $K_z$  profiles. SCAQS data should be used to test different mechanisms for prediction accuracy and to estimate several of the parameters required by the mechanisms.

Modeling Project 6: Emissions Inventory Grid Resolution. Simulations should be performed to assess the effect of the emissions inventory grid resolution on predicted concentrations. Grid nesting might be examined should finer resolution be called for in certain areas of the region.

- The Technical Support Division (TSD) of the Air Resources Board would like to use the SCAQS data in the development of control strategies for ozone and PM-10. Over the long-term, the data will also be useful for visibility, acid deposition, and toxic substance control strategy development as well. Specifically, given adequate resources, the TSD control strategy development tasks for O<sub>3</sub> and PM-10 would include the following steps.
  - Identify the characteristics of ozone and PM-10 episodes, and construct annual frequency distributions of these episodes.
  - Simulate the flow fields using wind models, and compare performance against wind measurements and tracer concentrations measured in SCAQS. Evaluate the performance of wind field models and improve them.
  - Develop a grid model with improved treatments of atmospheric chemical and physical processes, dry deposition, diffusion processes, and formation of nitrate, sulfate, and organic particles.
  - Apply the wind field and chemistry model to initial and boundary conditions acquired during SCAQS, and compare calculated values with those measured at SCAQS stations throughout the SOCAB. Evaluate the need for further model development.
  - Develop effectiveness factors for controls on particulate matter NO<sub>x</sub>, SO<sub>x</sub>, and hydrocarbons for each source type and receptor location.
  - Use cost-of-control figures, effectiveness factors, and PM-10 and ozone episode frequency distributions to derive cost-effective control strategies to reduce ozone levels and PM-10 levels throughout the SOCAB.
- General Motors Research Laboratories (GMR) will apply factor analysis techniques to estimate the major source contributions to PM-10 and PM-2.5 using the aerosol chemical composition data, routine gaseous pollutant data, meteorological data, emissions inventories, and emissions characterization results. GMR will also employ empirical and theoretical modeling to relate the chemical composition of the aerosol to the SCAQS visibility measurements using the chemical composition, impactor, visibility, and meteorological data. The mutagenic activity measurements will also be used in source apportionment models to identify their origins.

## 6.6 SYNTHESIS AND INTEGRATION OF SCAQS DATA INTERPRETATION RESULTS

The projects listed in Section 6.4 and 6.5 represent self-contained studies, yet to fully profit from the wealth of information in the SCAQS data, the results must be synthesized and presented in a cohesive form. A separate project, headed by the Data Analysis Coordinator, would provide this synthesis in the following manner. Projects 1.1, 1.2, and 1.3 would be performed first, and this descriptive information would be made available to all other researchers. Each researcher would use this information plus whatever he needs from the entire data base to perform the tasks specific to the project statement. All researchers would be known to each other, and communications



## 7. PROGRAM MANAGEMENT PLAN AND SCHEDULE

### 7.1 MANAGEMENT STRUCTURE

The SCAQS management structure is outlined in Figure 7-1. The major management functions are funded by ARB, and the Program Coordinator (PC) reports to the ARB. In a cooperative study such as this, however, the PC cannot have direct management authority over all phases of the study. In essence, his job is to manage by consensus, since direct fiscal responsibility will remain with ARB and the other sponsors for their respective contracts.

The PC receives guidance from a Management Advisory Group (MAG) consisting of representatives of the sponsors and technical advisors selected by the sponsors. The MAG decides the technical direction for the study. The principal role of the MAG is to ensure that the objectives of the study coincide with the needs of the sponsors and that the program plan is technically sound and is adequate to meet the objectives. This program plan has been prepared with the advice and approval of the MAG.

The PC works with the Field, Data, and Analysis Managers and ARB staff as a team to coordinate the activities of other ARB contractors. Although the PC does not have direct authority to manage the activities of participants funded by other sponsors, their decision to participate in the study and to follow the program plan should give the PC enough leverage to adequately manage the study.

During the study, the PC is responsible for the following tasks:

- Overall program coordination to keep the study on schedule and to resolve conflicts.
- Coordination of ARB contractor efforts.
- Coordination with the emissions contractor(s) and other complementary efforts.
- Coordination of quality assurance activities.
- Selection of sampling days.
- Monitoring achievement of defined milestones and periodic budgetary reviews to assure that the study goals can be met with the resources available.
- Periodic revision of the program plan to take into account technical, logistical, or budgetary issues or problems which might arise.
- Preparation of short periodic summaries of activities.
- Preparation of progress reports summarizing the progress, preliminary results, and conclusions to date of the study. These reports will require technical input from all participants.
- Coordination of periodic meetings of investigators.

- Coordination of a technical session or meeting at which the final study results will be presented and coordination of the submittal of manuscripts for back-to-back publication in a selected journal.
- Preparation of a final summary report which presents the results and conclusions of the study and provides a bibliography of SCAQS publications. The last two tasks are not funded at this time and may be performed by ARB staff.

The roles of the Field, Data, and Analysis Managers shown in Figure 7-1 have been described in previous sections. The Field Manager (FM) will prepare a measurement protocol with the input and review of the participants. The FM will be responsible for coordination of forecasting activities, assessing sampling readiness and for the day-to-day interactions with the field participants. The FM will also coordinate the preparation and upkeep of the A- and B-sites and related facilities. The actual work, however, will be performed by other contractors as indicated in Figure 7-1.

The DM will be responsible for the assembly, archiving, and distribution of all study data. The DM will also assemble and format data from supplementary sources with the help of the ARB staff.

The Analysis Coordinator (AC) will work with the investigators to assure that all objectives are addressed by one or more analysis efforts and to identify and eliminate redundant efforts. The AC will facilitate communications between investigators and encourage synergistic efforts.

Some boxes in Figure 7-1 are connected by dashed lines, indicating a consultative or coordination function. The Quality Assurance (QA) function is separate from the measurement functions and reports its results directly to the PC. The QA effort is coordinated by a QA Manager, but the actual QA work will be split among more than one contractor or sponsor. The activities of the QA Manager are defined in Section 4. His efforts are coordinated by the PC, but his reports will be independent documents from the reports prepared by the PC. Copies of the QA reports will be provided to participants and sponsors. It is the responsibility of the PC to find a way to remedy any serious program deficiencies identified by the QA Manager.

The Emissions, Meteorology, and Model Working Groups are independent committees of participants and sponsors. Some members of these groups are planning research efforts which provide input to or make use of the SCAQS data base. The Emissions and Model Working Groups have been set up to be complementary to SCAQS and their functions will continue beyond the SCAQS field program. The function of the Meteorology Working Group has been primarily to help design the SCAQS meteorology measurements, the forecast protocol and to help focus the tracer studies. The input of all three groups has been required in the design of SCAQS to ensure that the objectives can be met. The working groups provide their recommendations and input directly to the Program Coordinator and the MAG.

The day-specific emissions inventory function shown on Figure 7-1 is actually an activity which is designed and coordinated by the Emissions Working Group. The inventory contractor must coordinate closely with the field

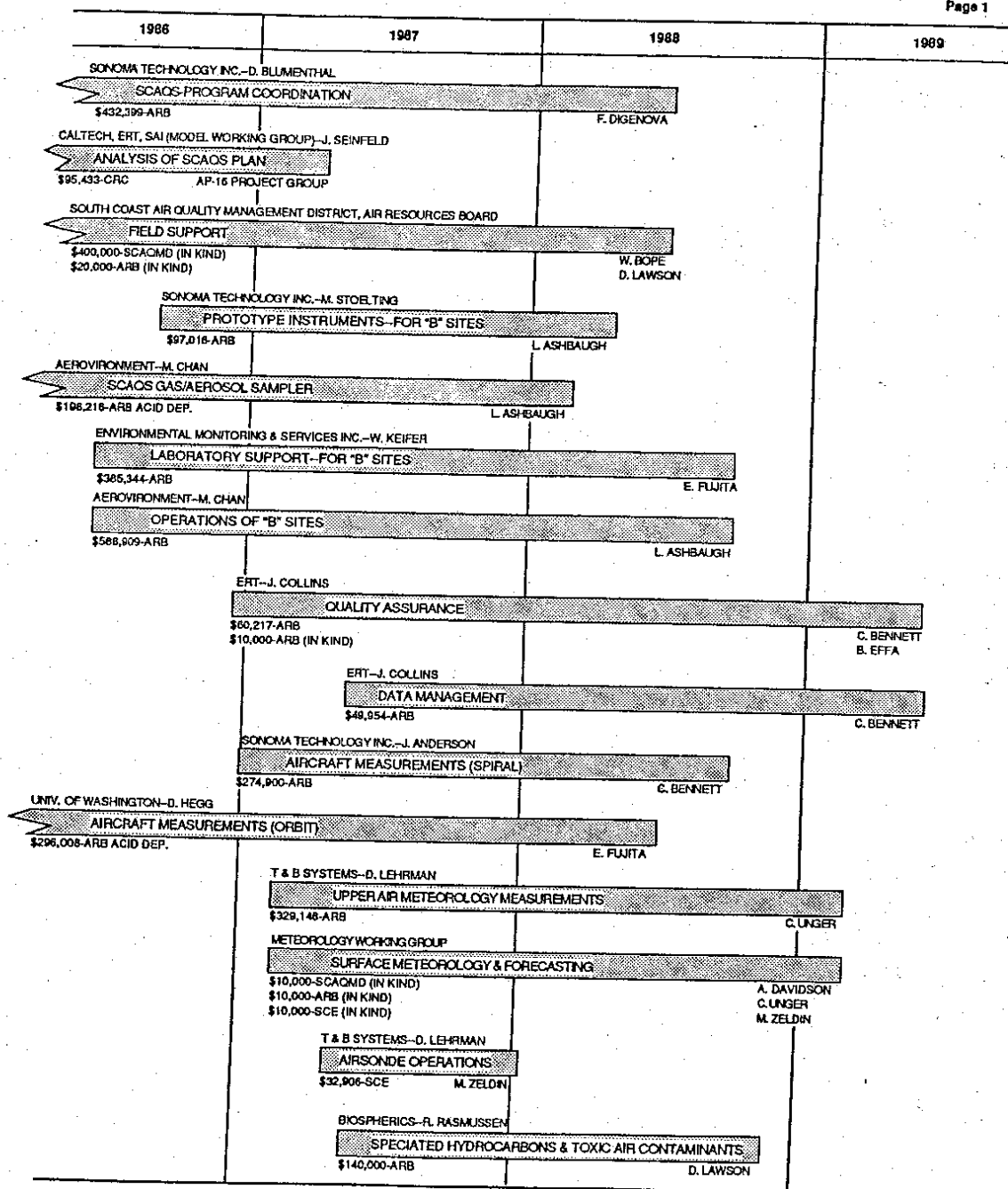


## 8. SCAQS FUNDING

SCAQS is a cooperative study which is being funded by many different government agencies, industry groups, and individual corporate sponsors. These include the California Air Resources Board (ARB), the Environmental Protection Agency (EPA), the South Coast Air Quality Management District (SCAQMD), the Coordinating Research Council (CRC), the Electric Power Research Institute (EPRI), the Ford Motor Company, the General Motors Research Laboratories (GMRL), the Motor Vehicle Manufacturers Association (MVMA), Southern California Edison (SCE), and the Western Oil and Gas Association (WOGA). The overall project is estimated to cost about nine million dollars. This estimate does not include future data analysis or modeling efforts.

Figure 8-1 gives a short summary of the contributions of the various sponsors. Figures 8-2 through 8-4 give a more detailed listing of individual contracts and in-kind contributions. The bars in Figures 8-2 through 8-4 show the general time scales of the contracts. The text around the bars indicates the organization performing the work, the principal investigator, the sponsoring organization, the contract manager, and the approximate cost of the contract or in-kind service. Since the study is in constant flux, some of the details in Figures 8-2 through 8-4 may change.

# Figure 8-2. SCAQS Core Program



(Continued)

Figure 8-3. SCAQS A-Site Studies

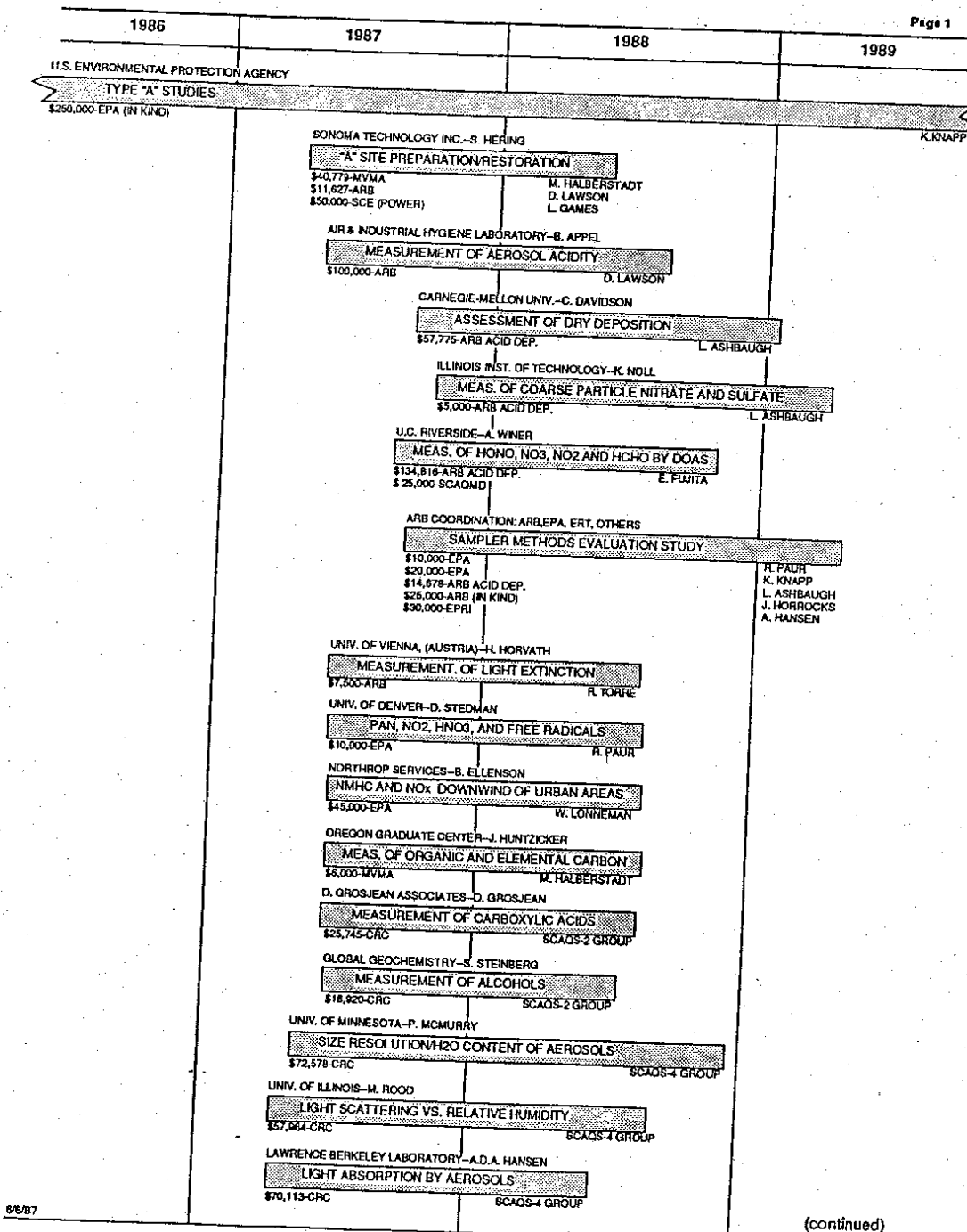
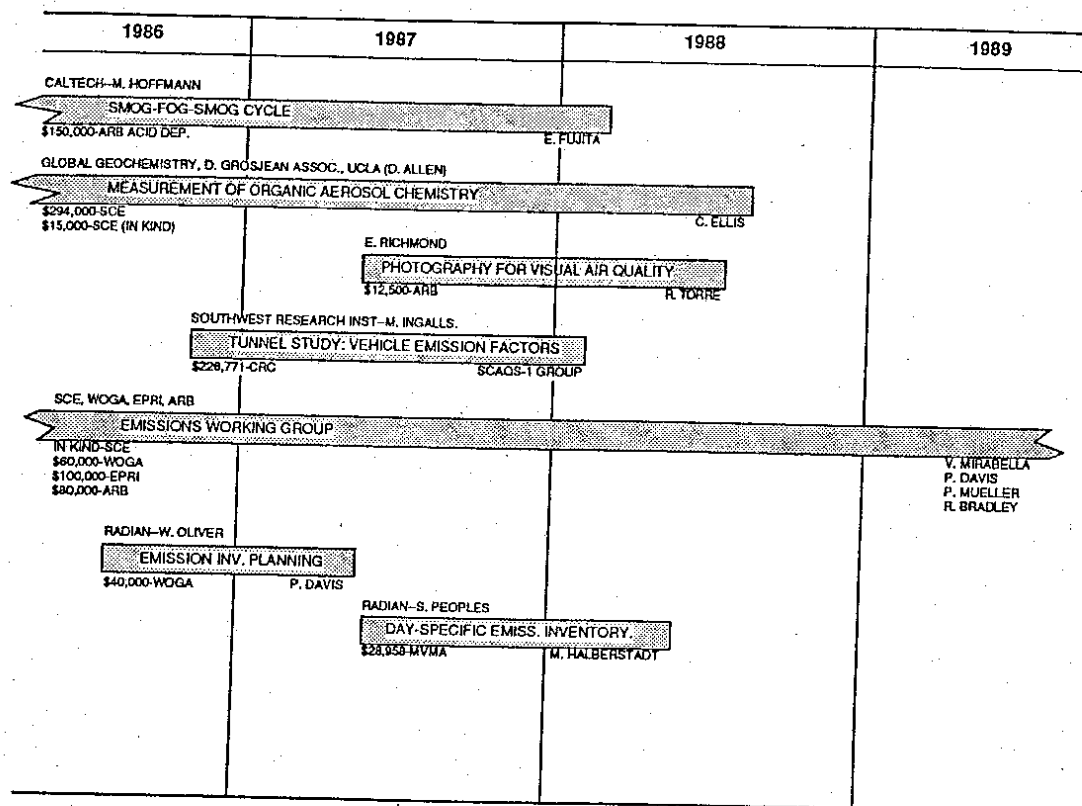


Figure 8-4. SCAQS Additional Studies



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## APPENDIX A. SCAQS PARTICIPANT AND MAILING LISTS

Many sponsors, participants, and potential users of the SCAQS data have contributed their ideas and their time for review and comment during the planning process. This Appendix includes lists of members of the SCAQS Management Advisory Group, of the SCAQS Technical Advisory Group, of the Emissions, Meteorology, and Model Working Groups, and of the CRC-APRAC SCAQS Coordination Group. Also included is a list of SCAQS projects and project managers and a current SCAQS mailing list.

Table A-3. Meteorology Working Group

<u>Members</u>	<u>Organization</u>
Art Davidson	SCAQMD Chairman
Chuck Bennett	ARB
Don Blumenthal	STI
Joe Cassmassi	SCAQMD
Frank DiGenova	ARB
Eric Fujita	ARB
Jack Horrocks	ARB
Bob Kessler	SAI
Bill Knuth	T&B Systems
Doug Lawson	ARB
Don Lehrman	T&B Systems
Frank Ludwig	SRI International
Stan Marsh	SCE
Ken Schere	EPA
Fred Shair	Caltech
Ted Smith	Ted B. Smith and Associates
Jack Suder	ARB
Mel Zeldin	SCE

Table A-4. Model Working Group

<u>Members</u>	<u>Organization</u>
John Seinfeld	Caltech Chairman
Praveen Amar	ARB
Roger Atkinson	UC Riverside
Glen Cass	Caltech
Tai Chang	Ford
Anton Chaplin	UnoCal (WOGA)
Alan Dunker	GM Research Laboratories
Michael Fosberg	US Forest Service
Robert Kessler	SAI
Chung Liu	SCAQMD
Alan Lloyd	ERT
Fred Lurmann	ERT
Vince Mirabella	SCE
Andrew Ranzieri	ARB
Philip Roth	WOGA
Kenneth Schere	EPA
Christian Seigneur	Bechtel
Christine Sloane	GM Research Laboratories
Thomas Tesche	Radian
Gary Whitten	SAI

Table A-7. SCAQS PROJECTS AND PROJECT MANAGERS

2006/P373-A01

6/6/87		PROJ. MANAGER/PRIN. INVESTIGATOR	
ORGANIZATION	FUNCTION	Name	Phone
ARB	Project Officer, QA audits, trailer, etc	Doug Lawson	(916) 324-8496
EPA	HC gases, XRF, etc	Ken Knapp	(919) 541-3085
SCAQMD	B-sites, C-sites, QA audits, etc	Bill Bope	(818) 572-6398
SCAQMD	Forecasting, Meteorology Working Group	Art Davidson	(818) 572-6421
AeroVironment	SCAQS sampler design, construction; B-site oper.	Mike Chan	(818) 357-9983
AIHL	Acid deposition studies	Bruce Appel	(415) 540-2477
AIHL	Berner Impactor & chemistry	Walter John	(415) 540-2644
ARB	Acid sampling methods comparison	Lowell Ashbaugh	(916) 445-0753
ARB-EI Monte	Long Beach B-site, acid sampling	John Kowalski	(818) 575-6856
Biospherics	Canisters for HC analysis, QA; toxics	Rei Rasmussen	(503) 690-1077
Caltech	Fog/smog/fog studies	Michael Hoffmann	(818) 356-4391
Caltech	Model Working Group	John Seinfeld	(818) 356-4635
Caltech	Tracer studies	Fred Shair	(818) 356-6811
Carnegie-Mellon U	Dry deposition measurements	Cliff Davidson	(412) 268-2951
Daniel Grosjean & Asso.	Organic acids, PAN	Daniel Grosjean	(805) 644-0125
DRI	Acid sampling	John Bowen	(702) 972-1676
DRI	Long range transport from LA	David Rogers	(702) 972-1676
DRI/STI	Aerosol water content	Fred Rogers	(702) 972-1676
EMSI	Analysis Coordinator	John Watson	(702) 972-1676
EMSI-BNL	SCAQS sampler analysis, B-site data vol	Bill Keifer	(805) 388-5700
EPA/Northrop	H2O2 @ B-sites	Miriam Lev-On	(805) 388-5700
EPA/Northrop Services	Acids and organic toxics	Bill Lonneman/Ellenson	(919) 541-2829
EPA/LV	XRF elements	Bob Kellogg	(919) 541-2895
ERT	LIDAR aircraft	Jim McElroy	(702) 798-2260
ERT	Aerosol carbon, carbonyls, acid species, PAN	Kochy Fung	(805) 499-1922
Ford	Quality Assurance Manager, Data Manager	John Collins	(805) 499-1922
Global Geochem	Spectrophone	Karen Adams	(313) 594-2612
GM Research Labs	Alcohols, carbon 14	Bob Gordon	(818) 992-4103
Illinois Inst of Tech	A/B van, special PM-10, captive air studies, etc	George Wolff	(313) 986-1599
LBL	Coarse particle measurements	Ken Noll	(312) 567-3538
OGC	Aerosol absorption	Tony Hansen	(415) 486-5319
Radian	Continuous aerosol carbon	James Huntzicker	(503) 690-1072
S W Research	Day-specific emissions	Bill Oliver	(916) 362-5332
SCE	Motor vehicle emissions study	Mel Ingalls	(512) 522-2645
SCE	Power at A-sites, organic aerosol measurements	Carol Ellis	(818) 302-1866
SCE	Tracer Study, met. soundings, forecasting	Stan Marsh/Mel Zeldin	(818) 302-2272
STI	Emissions Working Group	Vince Mirabella	(818) 302-6593
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STI	Field Manager	Susanne Hering	(213) 206-6193
STI	Spiral aircraft	Jerry Anderson	(707) 527-9372
STI	Long path light extinction by radiance difference	Will Richards	(707) 527-9372
T & B Systems	Upper air soundings	Don Lehrman	(707) 526-2775
Unisearch	Continuous H2O2	Gervase Mackay	(416) 669-2280
UC Davis	Drum impactors for elements, babs by LIPM	Tom Cahill	(916) 752-1120
UC Riverside	HONO and NO3 by DOAS	Arthur Winer	(714) 787-4651
UCLA	Impactor SO4, NO3, FTIR	David Allen	(213) 206-0300
UCLA	Impactor Pb, dichots	Sheldon Friedlander	(213) 825-2206
Univ. of Denver	Acid sampling	Don Stedman	(303) 871-3530
Univ. of Illinois	Temperature/RH nephelometer	Mark Rood	(217) 333-6963
Univ. of Minnesota	MOUDI impactor for carbon, aerosol water	Peter McMurtry	(612) 625-3345
Univ. of Vienna	Light ext by telephotometer	Helmut Horvath	
Univ. of Vienna	Detailed fine particle size distr.	Axel Berner	
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Table A-8. (continued)

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APPENDIX B  
SUMMARY OF AIR QUALITY STUDIES



## Summary of Selected Past South Coast Air Basin Studies (cont'd)

<u>Study Objectives</u>	<u>Sampling Site/Location/Period</u>	<u>Observables</u>	<u>Model Used</u>	<u>Major Findings</u>
<p>Reference: Hidy et al. (1975), Topics: Aerosol, Visibility</p> <p>To characterize the chemical &amp; physical properties of urban and non-urban aerosols</p> <p>To attribute ambient concentrations to primary &amp; secondary pollutant sources</p> <p>To identify major causes of production &amp; visibility reduction</p> <p>To estimate the extent of ambient air quality standards that can be achieved by existing technologies</p> <p>To evaluate the applicability of aerosol instrumentation in the study for use in monitoring networks</p> <p>To elucidate the photochemistry of aerosol formation</p>	<p>12 sites for mobile labs-Berkeley, Richmond SFOAF, Fresno, Hunter-Liggett Military Reservation, Freeway Loop, Pomona, Goldstone, Pt. Arguello, W. Covina, Robidoux (Riverside), and Domingue Hills</p> <p>July to Nov. 1972 July to Oct. 1973</p>	<p>Aerosols</p> <p>Total aerosol number concentrations</p> <p>Aerosol size distribution</p> <p>Size and chemically classified particles</p> <p>Light scattering</p> <p>Liquid water content</p> <p>Particulate fallout mass and organics</p> <p>Gases (SO<sub>2</sub>, H<sub>2</sub>S, NO, NO<sub>2</sub>, NH<sub>3</sub>, Total HC, HC, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO and O<sub>3</sub>)</p> <p>Meteorology (WS, WD, T°, RH, radiation and rainfall)</p>	<p>Descriptive graphical &amp; statistical methods</p> <p>Several models applied to data by other researchers</p>	<p>Found simplified approaches for the study of atmospheric particles</p> <p>Showed urban and rural aerosol mass is probably distributed bimodally in small (dp&lt;3 µm) and large (3µm&lt;dp&lt;20µm) plus giant (dp&lt;20 µm) particles</p> <p>Discovered that the two mass modes have independent sources and interact minimally in the atmosphere</p> <p>Found that particles formed by chemical reactions in the atmosphere add to the small particle size mode</p> <p>Pioneered the application of receptor models</p>

## Summary of Selected Past South Coast Air Bas In Studies (cont'd)

<u>Study Objectives</u>	<u>Sampling Site/Location/Period</u>	<u>Observables</u>	<u>Model Used</u>	<u>Major Findings</u>
<p>Reference: Henry and Hidy (1979), Topic: Sulfate</p> <p>To empirically identify the underlying chemical and physical process for sulfate production</p> <p>To apply a principal components model which is unaffected by intercorrelations of the variables</p>	<p>Southern California sites: Anaheim, Garden Grove, Glendora, Santa Monica, Thousand Oaks, Vista, W. Covina, CA</p> <p>Jan. 1974 to Jan. 1975</p>	<p>24-hr TSP mass</p> <p>Gases (SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, NMHC, Total HC)</p> <p>Meteorological variables (RH, temp, WS, WD, Inversion, ventilation)</p>	<p>Regression on principal components</p>	<p>Photochemical processes, SO<sub>2</sub> sources and atmospheric dispersion and transport are the three major causes of southern California sulfate levels</p> <p>Photochemical activity variance of (17-32%) and atmospheric moisture content variance of (9-15%) account for more than half of the sulfate variability</p>

## Summary of Selected Past South Coast Air Basin Studies (cont'd)

<u>Study Objectives</u>	<u>Sampling Site/Location/Period</u>	<u>Observables</u>	<u>Model Used</u>	<u>Major Findings</u>
<p>Reference: Cass and McRee (1983), Topic: Aerosol</p> <p>To develop better source apportionment techniques</p> <p>To assess the effects of different model structures on estimated source contributions</p>	<p>5 SCAQMD sites: Azusa, Lynwood, Pasadena, Reseda, W. Los Angeles</p> <p>5 NASN sites: Anaheim, Lennox, Los Angeles, Pasadena, San Bernardino</p> <p>1976 to 1977</p>	<p>24-hr TSP mass</p> <p>Ions (<math>\text{SO}_4^{2-}</math>, <math>\text{NO}_3^-</math>, <math>\text{NH}_4^+</math>)</p> <p>Elements</p>	<p>Emission Inventory/Rollback</p> <p>Tracer solution to chemical mass balance receptor model</p> <p>Ordinary weighted least squares solution to the chemical mass balance receptor model</p> <p>Multiple linear regression</p>	<p>Emissions inventory for fine particle trace metals can be constructed by superimposing size and chemical source compositions (resulted from source test) onto conventional TSP inventory</p> <p>Identifying key tracer elements of emission sources is important and can be used as input to CMB Model, thereby compensating for the deficiency in HiVOL data</p> <p>Consistent results were yielded by model/model comparisons</p>

## Summary of Selected Past South Coast Air Basin Studies (cont'd)

Study Objectives	Sampling Site/Period	Observables	Model Used	Major Findings
Reference: Proffins et al. (1984), Topics: Carbon Measurements, Visibility Reduction	Duarte and Lennox	8-hr Particulate Mass	Thermal analysis	Major source contributions to the carbon containing component of the fine aerosol
To estimate primary and secondary carbon contributions at receptors	July, 1980 to May, 1981	HIVOL with cascade impactor ( $dp < 15 \mu m$ , $3.5 \mu m$ , $dp < 7.2 \mu m$ , and $dp < 3.5 \mu m$ )	Emission inventory scaling	
To calculate a visibility extinction budget for Los Angeles		Dichotomous sampler ( $3.5 \mu m < dp < 15 \mu m$ and $dp < 3.5 \mu m$ )	Regression analysis	
		Elements (PIXE) ions ( $NH_4^+$ , $SO_4^{2-}$ , $NO_3^-$ , $Cl^-$ )		Automobile 68% 36% Industrial Sources 12% 28%
		Organic compound (volatile carbon black carbon)		A high correlation ( $R=0.72$ ) was found between ozone and secondary carbon, and low correlation ( $R=0.65$ ) was found between sulfate and secondary carbon The carbon containing component was responsible for 27 and 44% of the incident light extinction at Lennox and Duarte, respectively

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